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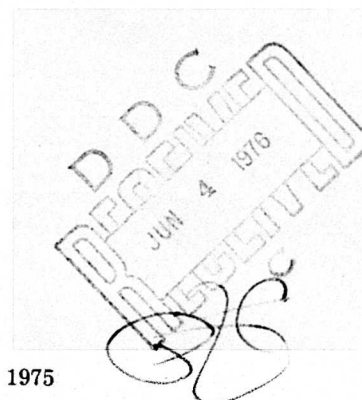
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AFML-TR-73-243

ADB011456

EXPLORATORY DEVELOPMENT OF
PROCESSABLE LAMINATING RESINS WITH
IMPROVED TOUGHNESS AND MODERATE
TEMPERATURE CAPABILITY
Volume III Phase II and III

JANUARY 1976

TECHNICAL REPORT AFML-TR-73-243, Volume III
FINAL REPORT FOR PERIOD JUNE 1974 - SEPTEMBER 1975



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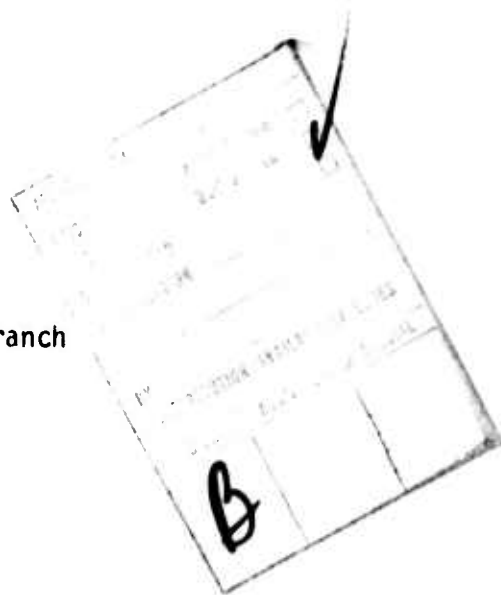
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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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18		19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
6		AFML TR-73-243 Vol 3		7 GOVT ACCESSION NO. 9	
10		EXPLORATORY DEVELOPMENT OF PROCESSABLE LAMINATING RESINS WITH IMPROVED TOUGHNESS AND MODERATE TEMPERATURE CAPABILITY. VOLUME III, PHASE II AND III.		11 TYPE OF REPORT & PERIOD COVERED Final Report, 1 June 1974 thru 30 Sep 1975	
		R. W. Vaughan, M. K. O'Rell and C. H. Snepard		12 PERFORMING ORG. REPORT NUMBER 22298-6042-TU-80	
		9 PERFORMING ORGANIZATION NAME AND ADDRESS TRW Systems, One Space Park, Redondo Beach, California 90732		13 CONTRACT OR GRANT NUMBER(S) 33615-72-C-2122	
		11 CONTROLLING OFFICE NAME AND ADDRESS AFML/MBC Nonmetallic Materials Division, Wright-Patterson AFB, Ohio 45433		14 PROGRAM ELEMENT PROJECT TASK AREA & WORK UNIT NUMBERS 16 HF 7340	
		14 MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12 REPORT DATE Jan 1976	
				13 NUMBER OF PAGES 37	
				15 SECURITY CLASS (of this report) Unclassified	
				15a DECLASSIFICATION DOWNGRADING SCHEDULE	
16 DISTRIBUTION STATEMENT (of this Report) Distribution limited to U. S. Government agencies only; Test and Evaluation; Jan 1976 Other requests for this document must be referred to the Air Force Materials Division, Composite and Fibrous Materials Branch, AFML/ MBC, Wright-Patterson AFB, Ohio 45433.					
17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)					
18 SUPPLEMENTARY NOTES					
19 KEY WORDS (Continue on reverse side if necessary and identify by block number) Composites DONA Polyimide Resins, Graphite Fibers, Polyimide Graphite Epoxy Graphite Hydrolytic Instability Mechanical Properties. High Humidity Aging Fracture Toughness					
20 ABSTRACT (Continue on reverse side if necessary and identify by block number) Resin optimization studies and adhesive development work were continued with the DONA polyimide resin developed under Phase I of this program. Objectives of the Phase II and III studies during this twelve-month period were to identify a lower boiling solvent than DMF or NMP and to develop an adhesive using the DONA poly- imide resin. The PMR approach (polymerization of monomeric reactants) was evalua- ted as a route to obtaining resin stability in low boiling solvents. It was de- monstrated that the use of DMF is key to obtaining sufficient imidization prior to cure at 400°F. Attempts to develop an adhesive using the DONA polyimide resin were unsuccessful.					

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FOREWORD

This report was prepared by TRW Systems Group, Redondo Beach, California, under Contract F33615-72-C-2122, "Exploratory Development of Processable Laminating Resins With Improved Toughness and Moderate Temperature Capability". The contract was initiated under Project No. 7340 and administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, with Mr. L. Picklesimer (AFML/MBC), Composites and Fibrous Materials Branch, Nonmetallic Materials Division, as the Project Engineer. Mr. R. W. Vaughan, Program Manager, directed the program at TRW Systems, Mr. M. K. O'Rell conducted the resin optimization studies and Mr. C. H. Sheppard performed the adhesive development work. Additional participants were Dr. R. J. Jones and Dr. G. A. Zakrzewski.

The report covers the period from 1 June 1974 through 30 September 1975. Two previous reports, AFML-TR-73-243, Volumes I and II, cover the period from 1 June 1972 through 1 June 1974.

The Contractor's report number is 22298-6042-TU-00.

The mention of commercially available products should not be construed in any way as an endorsement by the Government. Comparative information has been presented for the purpose of illustrating the influence of processing parameters on various materials and their properties.

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I. INTRODUCTION AND SUMMARY

This final report presents the work accomplished by TRW Systems for the Air Force Materials Laboratory Nonmetallic Materials Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, USAF under Phase II and III of Contract F33615-72-C-2122 during the period 1 June 1974 through 30 September 1975. The objective of this program was to develop new and improved resins and adhesives having processability equivalent to current state-of-the-art, moderately elevated temperature (up to 365°F) epoxy systems, but with a significantly higher resistance to moisture and a significantly higher degree of toughness.

The activities discussed herein are a continuation of the work performed under, Phase I (Reference 1), Phase II and Phase III (Reference 2). During the Phase I work a polyimide resin was identified which provided graphite fiber reinforced composites that did not undergo the same drastic elevated temperature mechanical property degradation after exposure to humid atmosphere as the currently available high performance epoxy resin systems. This resin was a TRW A-type polyimide resin similar to P105A developed under Contract F33615-70-C-1392 (Reference 3), but with 3,6-dimethyl-3,6-endoxy-1,2,3,6-tetrahydrophthalic anhydride (DONA) end-caps. The specific formulation selected during Phase I consisted of a 1200 formulated molecular weight (FMW) polyimide prepolymer of DONA/80 methylene dianiline (MDA): 20 thiodianiline (TDA)/bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA). The anticipated advantage of the DONA polyimide resin was that the reverse Diels Alder cure would occur at ~400°F. However, the results obtained during Phase I were not considered to be representative of the resin system when processed under optimum conditions. Specifically, DMF and NMP were the two solvents used during Phase I. Because both are high boiling it was difficult to remove them completely prior to resin cure. Consequently, during the first part of Phase II the primary objective was to identify a low boiling solvent for the DONA amide acid or polyimide prepolymer. The other objective was to identify a DONA polyimide resin formulation that did not contain TDA. This was necessary because TDA became unavailable commercially at the end of the Phase I

activities. During the Phase II and Phase III activities reported previously (Reference 2), a satisfactory resin formulation was identified which did not contain TDA. However, attempts to identify a lower boiling solvent than DMF or NMP for the DONA amide acid or polyimide prepolymer were unsuccessful.

Consequently, during the Phase II continuation activities reported herein, further attempts were made to identify a satisfactory low boiling solvent for the DONA polyimide resin. This work was concentrated on application of the PMR (polymerization of monomeric reactants) approach developed at NASA Lewis Research Center (Reference 4) to the DONA resin system. Also, evaluation of low boiling point azeotropes of NMP as solvents for the DONA polyimide prepolymer was performed. Potentially promising resins were screened by molding small graphite fiber reinforced composites. Because satisfactory results were not obtained during these studies, additional monomer and polymer characterization studies were performed in order to obtain an understanding of the chemistry and reaction kinetics involved in the DONA polyimide resin cure. This was necessary in order to assess the potential of the DONA polyimide resin for providing facile processability, *i.e.*, <400°F cure temperature and <100 psig molding pressure.

The Phase III adhesive work consisted of evaluating various adhesive formulations containing DONA polyimide resin. Approaches were employed similar to those developed under Contract NAS 1-9532 (Reference 5) where copolymer blends of polyimide and polyamide-imide resins were developed to provide a high temperature adhesive. Unfortunately, the cure temperature regions for the DONA polyimide resin and the AMOCO AI 1137 amide-imide resin used previously were incompatible. Consequently, a DONA polyamide-imide resin was conceptualized for future evaluation that could provide improved adhesion.

During this third twelve-month period of performance for this contract, TRW Systems performed the following tasks:

- PHASE II - COMPOSITE STUDIES
TASK I - RESIN OPTIMIZATION
- PHASE III - ADHESIVE STUDIES
TASK II - DEVELOPMENT OF ADHESIVES

This report is divided into sections covering the Resin Optimization and Adhesives Development work. The significant conclusions reached and assessments of the results are listed, as well as Appendices covering detailed descriptions of procedures used in material preparation, processing and testing.

II. RESIN OPTIMIZATION

During the third twelve-month technical effort on this program, it was determined that a polyimide prepolymer derived from *bis*[4-(3,4-dicarboxyphenoxy)phenyl] sulfone (BSDA), methylene dianiline (MDA) and dimethyloxynadic anhydride (DONA) showed promise as a laminating resin. Considerable effort was devoted during this time to the search for an acceptable solvent or solvent system other than DMF or NMP. The latter solvents were found to adversely affect the mechanical properties of the graphite reinforced composites derived from the DONA resin. Two different approaches were investigated for obtaining the desired improved solvent system. These approaches were a) formulation of a low boiling point azeotrope of NMP as a solvent for the DONA polyimide prepolymer, and b) application of the PMR (polymerization of monomeric reactants) approach developed at NASA Lewis Research Center (Reference 4) to the DONA resin.

The PMR approach was very appealing because it employs a combination of esters and amines in methanol solvent at a stoichiometry level to yield a given formulated molecular weight (FMW) prepolymer. The use of methanol as the solvent is very attractive because of its low boiling point.

When the PMR approach was applied to the DONA resin system, an immediate problem was encountered. It was found that the required monomethyl ester of DONA could not be prepared and isolated. Repeated attempts to prepare the ester resulted in the isolation of dimethyl fumarate and 2,5-dimethylfuran. The formation of these compounds was attributed to a reverse Diels-Alder reaction which occurred under very mild conditions. An expedient solution to this problem was the use of the DONA anhydride in a methanol solution of MDA and BSDA diester. The resultant varnish displayed very limited shelf-life (~4 hours) at which time the DONA-MDA amide acid precipitated. However, this system was employed to prepare a composite with marginal success. Consequently, studies were undertaken, first to identify solvents for the conventional DONA amine acid prepolymer approach and then to improve the toughness of the DONA resin using DMF as the solvent. When these attempts resulted in limited success, the PMR approach was selected for additional investigation.

2.1 EVALUATION OF DONA AMIDE ACID/METHYL CELLOSOLVE VARNISH

During the initial DONA PMR resin studies conducted during the third twelve-month technical effort, it was determined that methyl cellosolve (2-methoxyethanol) is a fairly good solvent for the constituents of the DONA resin. This solvent is fairly attractive from the standpoint of its boiling point ($\sim 257^{\circ}\text{F}$), flash point ($\sim 115^{\circ}\text{F}$), cost and toxicity. Consequently, it was decided to evaluate this solvent for preparing the conventional DONA amide acid prepolymer in place of DMF or NMP. The normal experimental procedure was employed to prepare the laminating varnish and is given in Appendix A. A prepreg was prepared from type A-S graphite fiber tow by dip-coating and drum winding at 8 tows per inch using 25% w/w resin solids solution. The first prepreg was allowed to dry on the drum overnight to give an unhandleable prepreg with $\sim 2\%$ w/w residual solvent.

Further studies defined that 10-15% volatile content was necessary to obtain the desired prepreg handleability. A tape with 14% w/w volatile content was laid-up into a 10-ply stack and molded using the following cycle:

- 30 minutes at 160°F at ~ 7 psia vacuum bag pressure
- 45 minutes at 180°F at ~ 7 psia vacuum bag pressure
- Heat to 250°F , then apply full vacuum bag pressure (~ 14 psia) plus 50 psig positive gas pressure for 90 minutes
- Heat to 400°F , then increase pressure to 100 psig for 120 minutes
- Cool to R.T., remove composite and postcure at 475°F for 16 hours.

Properties for the molded composite are given in Table 1 and appeared promising. The shear strength, however, were lower than desired.

TABLE 1.
PROPERTIES OF INITIAL DONA/A-S GRAPHITE COMPOSITE FROM
AMIDE ACID/METHYL CELLOSOLVE VARNISH

Property	Value
Flexural Strength, Ksi	
at R.T.	165
at 365°F	129
Strength Retention, %	78
Flexural Modulus, Msi	
at R.T.	18.0
at 365°F	17.6
Modulus Retention, %	97
Shear Strength, Ksi	
at R.T.	8.2
at 365°F	5.8
Strength Retention, %	71

Two additional composites (5-inch x 5-inch) then were fabricated to determine reproducibility of the process. The slightly modified process cycle was as follows:

- 60 minutes at 125°F at ~7 psia vacuum bag pressure
- 40 minutes at 180°F at ~7 psia vacuum bag pressure
- Heat to 250°F, then apply full vacuum bag pressure, (~14 psia) plus 50 psig positive gas pressure for 60 minutes
- Heat to 400°F, then increase pressure to 100 psig for 120 minutes
- Cool to R.T., remove composite and postcure in air at 475°F for 16 hours.

Properties for the composite are given in Table 2. The low mechanical properties (Table 2) were surprising in view of the promising results obtained from the initial composite fabrication. It was evident that the process was not optimized and that considerable effort would be required to determine the optimum process cycle.

Additionally, the varnish displayed an undesirably short shelf-life (~4 hours). Based on these results, it was decided to discontinue the work with methyl cellosolve and to use DMF in order to expedite evaluation of DONA polyimide resins formulated at various molecular weights.

TABLE 2.
PROPERTIES OF DONA/A-S GRAPHITE COMPOSITE FROM
AMIDE ACID/METHYL CELLOSOLVE VARNISH

PROPERTY	EXPERIMENT #1	EXPERIMENT #2
Flexural Strength, Ksi		
at R.T.	88	71
at 365°F	57	53
Flexural Modulus, Msi		
at R.T.	16.6	15.8
at 365°F	17.3	16.3
Shear Strength, Ksi		
at R.T.	3.9	4.1
at 365°F	3.9	3.9
Density, g/cc	1.56	1.56
Fiber Volume % v/v	62.7	62.5
Void Content % v/v	1.1	1.1

2.2 EVALUATION OF HIGHER FORMULATED MOLECULAR WEIGHT DONA PREPOLYMER

A major objective of this program was the development of a resin matrix possessing increased toughness over state-of-the-art materials. Initial fracture toughness determinations revealed that DONA/A-S composites provide lower fracture toughness values than epoxy/A-S composites. Consequently, a preliminary evaluation of higher molecular weight formulations (*i.e.*, when $n = >1$) was performed in an attempt to obtain composites with greater fracture toughness.

The higher molecular weight DONA prepolymer was formulated to yield a molecular weight of 1960 ($n = 2$) using the normal formulary techniques. The 40% w/w resin solids varnish in DMF was doctored onto Hercules Type A-S graphite fiber, then dried for two hours by a heat lamp and two hours

in an air circulating oven at 200°F. A panel was prepared by the following cycle:

- Heat 60 minutes at 230°F under 15 psig vacuum bag pressure
- Heat for 60 minutes at 300°F, apply pressure to 80 psig and raise temperature to 400°F for 60 minutes
- Cool to R.T. and postcure in air at 475°F for 16 hours.

The resultant composite had flexural strength values of 165 Ksi at room temperature and a room temperature shear strength value of 8.5 Ksi.

Several additional molding cycles then were evaluated in order to assess the potential of higher molecular weight resins.

The most promising autoclave cycle developed was the following:

- Heat to 230°F for 30 minutes under 15 psig vacuum bag pressure
- Apply 30 psig positive pressure, heat to 250°F for 30 minutes, then raise the temperature to 300°F for 60 minutes
- Raise pressure to 80 psig and temperature to 400°F for 60 minutes
- The finished composite was cooled to R.T. and post-cured in air at 475°F for 16 hours.

The composite panels obtained from this process appeared to have low void content after the autoclave cycle, but blistered badly during postcure. The massive outgassing which generated the interlaminar voids was attributed to retention of DMF, but may also have resulted from some end-group degradation of the resin. However, void formation during postcure appeared to be greater for the panels prepared from the higher

molecular weight resin which would tend to support the premise that DMF was the major cause of void formation. In light of these results, it was deemed appropriate to concentrate the technical effort on the development of the PMR approach for the DONA resin.

2.3 DONA PMR TECHNOLOGY DEVELOPMENT

In studies conducted earlier in the program, which were reviewed in Section 2.1, it was shown that a DONA PMR laminating varnish could be prepared in methanol and a prepreg prepared from the varnish possessed good handleability. However, the DONA PMR resin system failed to give consistently good composites by autoclave processing and, in addition, the PMR varnish in methanol possesses a very limited shelf-life (~2 hours). Consequently, the studies conducted in this investigation were aimed towards developing an improved DONA PMR resin which would furnish acceptable, reproducible laminates and a laminating varnish with increased shelf-life.

2.3.1 Solvent Screening Study

As the first step in developing an improved DONA PMR resin, a solvent screening study was conducted to identify low boiling solvents other than methanol for the preparation of a laminating varnish from the DONA-MDA amide-acid and the dimethyl ester of BSDA.

The solvent screening study included solvents (see Table 3) from each of the following classes: alcohols, ketones, esters and ethers. The solvents were screened by preparing a solution of MDA and DONA in the candidate solvent under a nitrogen atmosphere. The solutions then were periodically checked for precipitate formation while standing at room temperature. All of the solutions prepared from these solvents showed precipitate formation within 2 hours. The precipitate was isolated by filtration and was found to be the MDA-DONA amide-acid by ir analysis. Because order of addition of solutes to solvent can drastically affect solubility, the solvents also were evaluated by first adding the dimethyl ester of BSDA followed by the addition of MDA and DONA. The diester failed to enhance

the solubility of the MDA-DONA amide-acid and a precipitate was observed within two hours of initial mixing. Consequently, this approach to a DONA PMR laminating resin was abandoned and a new approach was investigated as described below.

TABLE 3.
SOLVENTS SCREENED FOR USE AS DONA PMR LAMINATING SOLVENT

Solvent Class	Solvent
Alcohol	Methanol Ethanol
Ketone	Acetone
Ester	Ethyl Acetate
Ether	THF Dioxane
Mixtures	Methanol/Dioxane

2.3.2 Diamine Screening Study

The problem encountered when the PMR approach was applied to the original DONA resin was precipitation of the MDA/DONA amide acid. As was discussed in the preceding section, this problem was not corrected by changing the solvent system. The next approach selected for investigation was to assess whether the DONA-amide acid of other aromatic diamines were more soluble in methanol or other low boiling solvents than the DONA-MDA amide acid.

The screening study was conducted by preparing a DONA PMR solution from DONA, BSDA diester and the candidate diamine in methanol under a nitrogen atmosphere at 40% w/w solids. The solutions then were allowed to stand at room temperature and the time at which precipitation occurred was recorded. The results of the study are presented in Table 4. The one promising candidate identified in this work was 3,3'-sulfonyldianiline; the other diamines behaved in a similar fashion to MDA, that is, a

precipitate formed within two hours. The *m,m'*-diaminobenzophenone candidate was not soluble in methanol.

TABLE 4.
DIAMINES SCREENED FOR USE IN DONA PMR APPROACH

Diamine	Time at Which Precipitation Observed, ^{a)} Min.
<i>m,m'</i> -MDA	120
<i>m,m'</i> -diaminobenzophenone	Not soluble
4,4'-oxydianiline	90
4,4'-sulfonyldianiline	90
3,3'-sulfonyldianiline	No precipitate

^{a)}Solutions prepared in methanol at 40% w/w solids.

Additional characterization studies then were conducted on the *m,m'*-sulfonyldianiline containing DONA PMR resin. A sample of the varnish was aged at room temperature for 10 days and no precipitate was observed. After this time period, a sample of the varnish was dried and the resultant resin was characterized for its flow/cure properties after being staged at various temperatures. This information was desired for 1) structuring a processing cycle for the resin and 2) to see how the new resin compared (e.g., melt/flow) to the original DONA PMR prepared from MDA. The resin was subjected to the experimental conditions shown in Table 5. At the end of each isothermal heating cycle, a sample of the resin was characterized by infrared spectroscopy (ir) and by its melt flow characteristics when placed on a preheated (400°F) Fisher-Johns melting point apparatus.

TABLE 5.
INITIAL CHARACTERIZATION OF STAGED *m,m'*-SULFONYL-
DIANILINE CONTAINING DONA PMR RESIN

Staging Temp. °F	Staging Time, Min.	Intensity Imide Bands in ir Spectrum	Melt/Flow at 400°F
185	30	None	Yes
250	30	Very weak	Yes
300	30	Moderate	Yes
340	30	Strong	Very little

A larger sample of the DONA PMR resin was prepared by allowing methanol to evaporate from a freshly prepared varnish (40% w/w solids). The sample so isolated was partially imidized by heating it at 290°F for two hours in a forced-air oven. The prepolymer then was cured for two hours at 400°F under 200 psi pressure. The sample obtained from this experimentation was powdered and subjected to thermogravimetric analysis (TGA) to assess its initial thermo-oxidative stability. The polymer displayed a 3% weight loss at 400°F and thereafter a gradual weight loss (25% total loss) out to 800°F before the sharp break occurred. This result was attributed to possible incomplete cure of the resin after two hours at 400°F.

Subsequently, a portion of the cured sample then was postcured at 400°F for four hours in an attempt to improve its thermo-oxidative stability by further curing the resin. The TGA on the postcured sample showed a slight increase in thermo-oxidative stability but the gradual weight loss (total of 20%) from 400°F to 800°F still was present, although somewhat reduced. These results were surprising in view of the results obtained on the original DONA resin investigated in Phase I of the program (Reference 3). The original DONA resin displayed an initial thermo-oxidative stability of 660°F with little weight loss up to 660°F.

It then was decided to evaluate variations to the cure cycle to ensure that the prepolymer was allowed sufficient time to become fully formed and imidized prior to cure. A sample of the prepolymer was first heated at 350°F for 30 minutes; then the temperature was raised to 400°F over a 20-minute period. The sample then was cured for two hours at 400°F under 30 - 40 mm Hg pressure (water aspirator vacuum to simulate vacuum conditions in an autoclave). The resultant polymer displayed a first break in the TGA at 554°F, i.e., ~100°F improvement in thermo-oxidative stability. A second sample was cured in an identical fashion except that the cure cycle was extended to six hours. This sample exhibited the same thermo-oxidative stability as the sample cured for two hours.

The two samples then were postcured as powders in a forced-air oven at 450°F for 24 hours. The recorded weight losses during postcure were ~1.5% (w/w). TGA analysis of the postcured samples showed a slight increase in thermo-oxidative stability (580°F). The postcured samples then were assessed for long-term thermo-oxidative stability by isothermally aging them at 365°F in a forced-air oven. The isothermal aging results (see Table 6) indicated that the new DONA PMR resin was stable at 365°F and would meet program objectives. Based on these results, composite fabrication studies were initiated using the DONA PMR laminating resin.

TABLE 6.
ISOTHERMAL AGING RESULTS ON DONA PMR RESIN AT 365°F

Cure Duration, ^{a)} hr	Weight Loss, %		
	Time, hr		
	72	120	168
2	0.7	1.4	1.4
6	0.6	1.3	1.4

^{a)} Other cure conditions; 400°F at 30 - 40 mm pressure, post-cured at 450°F for 24 hours.

2.3.3 Composite Fabrication Studies Using DONA PMR Resin Varnish In Methanol

A 5-inch wide Type A-S graphite fiber prepreg tape was drum wound using the DONA-PMR resin (30% w/w) in methanol. After overnight drying on the drum, the tape was cut into pieces, 5-inch by 5-inch. A nine-ply composite was made using the following cycle:

- Prepreg dried for one hour at 150°F
- Lay-up placed in a vacuum bag
- Heated to 180°F under 10 psia vacuum bag pressure and heated for 60 minutes
- Temperature increased to 250°F, 30 minutes dwell, and then temperature was raised to 350°F
- At 350°F, full vacuum and an additional 50 psig pressure was applied. A dwell time of 15 minutes at 350°F was used.
- The pressure was augmented to 100 psig for an additional 15 minutes dwell time at 350°F
- The composite was heated to 400°F for an additional 4 hours
- The finished part was cooled to R.T., and postcured in air for 1 hour at 425°F, followed by 16 hours at 450°F.

The resultant unidirectional composite exhibited excessive resin flow and the room temperature flexural strength values were ~80 Ksi. Consequently, a second unidirectional composite then was made using a modified cure cycle to decrease the resin flow prior to onset of polymerization. In this cure cycle, an additional 30 minutes dwell time was used at 320°F for polymerization of the monomers to form the prepolymer and 100 psig pressure was applied as soon as the composite reached 350°F for consolidation of the part. A 60-minute dwell time was utilized at 350°F prior to the 4-hour, 400°F cure. The same postcure cycle was used as for the first composite. No blistering was observed before or after postcure of either composite and the properties of the second laminate are given in Table 7.

TABLE 7.
PROPERTIES OF DONA-PMR TYPE A-S GRAPHITE FIBER
POLYIMIDE LAMINATE

Flexural Strength, Ksi at P.T.	120
Shear Strength, Ksi at P.T.	3.2
Density g/cc	1.44
Fiber Volume % v/v	68
Void Content % v/v	10.5

Although the resin content for the second laminate was reasonable, the excessive void formation substantially decreased the mechanical properties of the composite. At this point, it is obvious that further modification of the cure cycle was necessary in order to obtain reasonable resin levels in the composite with decreased void content. Consequently, before continuing with the composite processing studies, it was decided to conduct additional resin studies as described below.

2.3.4 Additional Cure Studies of DONA PMR Resin

These studies were conducted with the intent of further defining the cure chemistry of the DONA-PMR resin. Information gained from this study was intended for use in structuring autoclave molding cycles for additional composite fabrication studies.

To conduct the studies, a 30% (w/w) solids varnish was prepared from 3,3'-sulfonyldianiline, DONA and the dimethyl ester of BSDA at $n = 1$ formulated molecular weight. The solvent then was allowed to evaporate and the residue was heated at 175°F for one hour and then at 212°F for one hour. The resultant material was introduced into the pyrolysis unit and cured under vacuum (~40 torr) according to the following cycle:

Temperature	Time
250°F	0.5 hour
320°F	0.5 hour
350°F	0.5 hour
400°F	4 hours

The cured resin was characterized by TGA by heating to 400°F and then holding at that temperature for 4 hours before continuing the scan out to decomposition. This procedure was adopted to determine if additional volatile matter was evolved from the cured resin, and if so, the amount. Any volatile formation, after cure, greatly increases the probability of void formation in composites.

The TGA results (see Figures 1 and 2) showed that 0.5% w/w weight loss occurs up to ~527°F, which indicates little volatile matter formation. However, a powdered sample of the cured resin heated at 400°F in a forced-air oven was observed to soften and partially coalesce. This observation was attributed to incomplete cure of the resin after 4 hours at 400°F. Consequently, a second sample of the prepolymer was subjected to an extended longer cure cycle as follows:

250°F	0.5 hour
320°F	1 hour
350°F	1 hour
400°F	8 hours

TGA results for this sample were identical to those obtained for the previous sample, *i.e.*, ~0.5% w/w weight loss occurs up to ~525°F. However, a powdered sample heated at 400°F appeared to remain mostly as a powder, and had coalesced to a lesser degree than observed above. Thus, it appeared as though a longer time at 400°F provided a higher degree of cure.

Since this chemical behavior of the DONA PMR resin was considerably different than that observed for the original DONA system, it was postulated that the methanol solvent was causing incomplete cure.

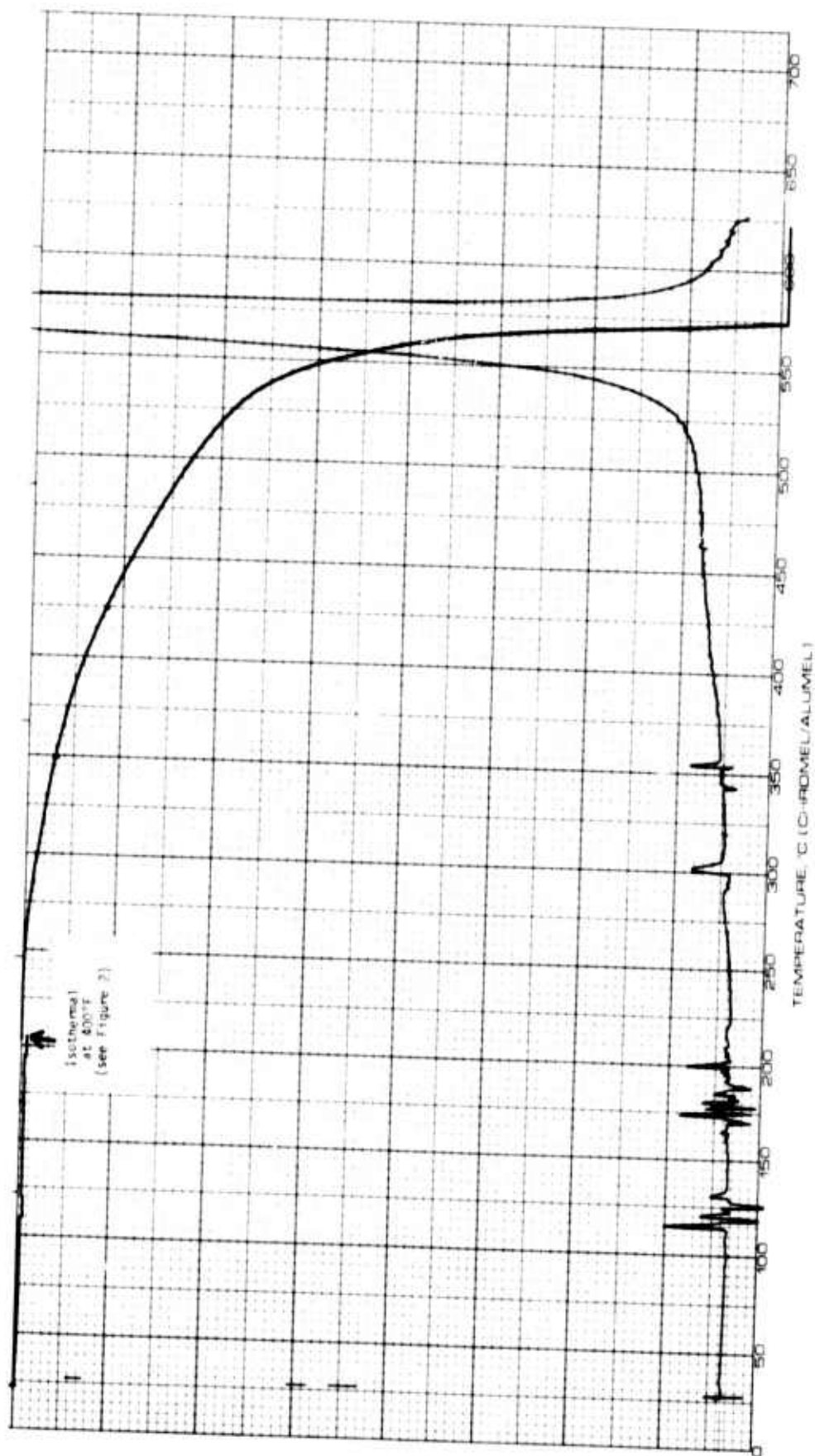


Figure 1. TGA Curve For Cured DONA PMR Resin Prepared In Methanol

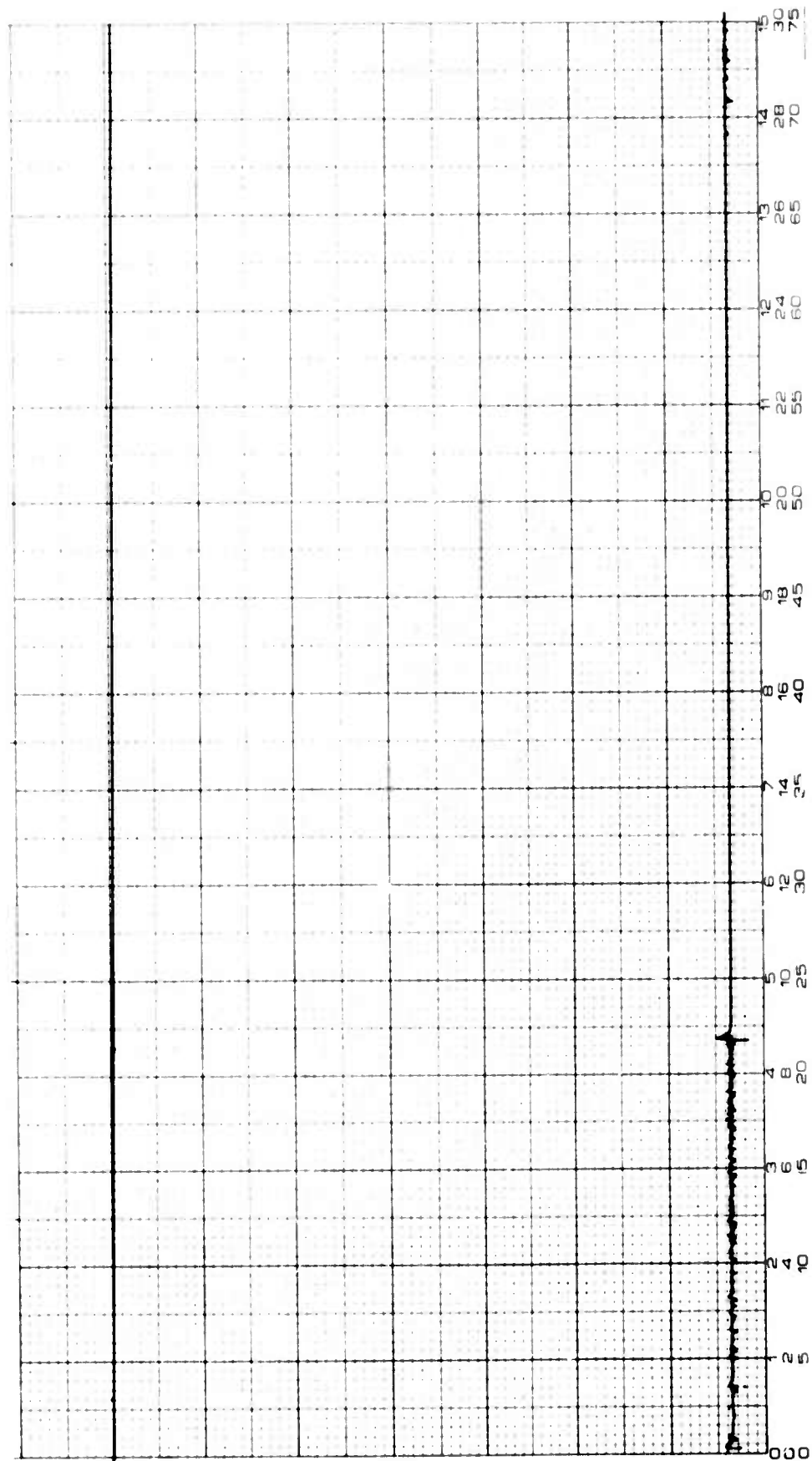


Figure 2. Isothermal TGA (400°F) For Cured DONA Resin

Therefore, additional cure studies were conducted on the DONA-PMR resin using acetone as the solvent. The same experimental conditions were employed as for the studies using methanol. That is, a 30% (w/w) solids varnish was prepared from 3,3'-sulfonyldianiline, DONA and the dimethyl ester of BSDA. The solvent was allowed to evaporate (simulating prepreg fabrication conditions) and the resultant residue was heated at 175°F for one hour and at 212°F for one hour. The "staged" prepolymer then was cured under vacuum (~40 torr) according to the following cycle:

Temperature	Time
250°F	0.5 hour
320°F	1 hour
350°F	1 hour
400°F	4 hours

Characterization of the cured resin by TGA (see Figure 3) showed the same behavior for this resin as was observed for the DONA-PMR resin derived from methanol. Decomposition was observed at 525°F and 2.0% w/w to weight loss occurred up to decomposition. A powdered sample of the resin subjected to 400°F for 8 hours was observed to soften and coalesce partially. These results indicated that little or no advantage was gained in using acetone in place of methanol as the laminating solvent.

One important piece of information that was lacking for this new DONA system (*i.e.*, prepared using 3,3'-sulfonyldianiline rather than MDA) was its cure behavior when prepared in DMF. This information was required before the unusual results obtained on the PMR approach could be attributed to solvent and not the new diamine. Consequently, a sample of the DONA prepolymer was prepared at $n = 1$ in DMF at 30% (w/w) solids from 3,3'-sulfonyldianiline, BSDA and DONA. A sample of the amide acid was isolated by removing solvent *in vacuo* at 176°F. The infrared spectrum of this prepolymer sample is shown in Figure 4. It is evident from the spectrum that the prepolymer is in the amide acid form with a small amount of imide present (*i.e.*, imide carbonyl band at 1775 cm^{-1}). The prepolymer then was cured at 400°F for 4 hours and the resultant polymer was subjected to thermogravimetric analysis. The TGA was run as follows: heated to 400°F

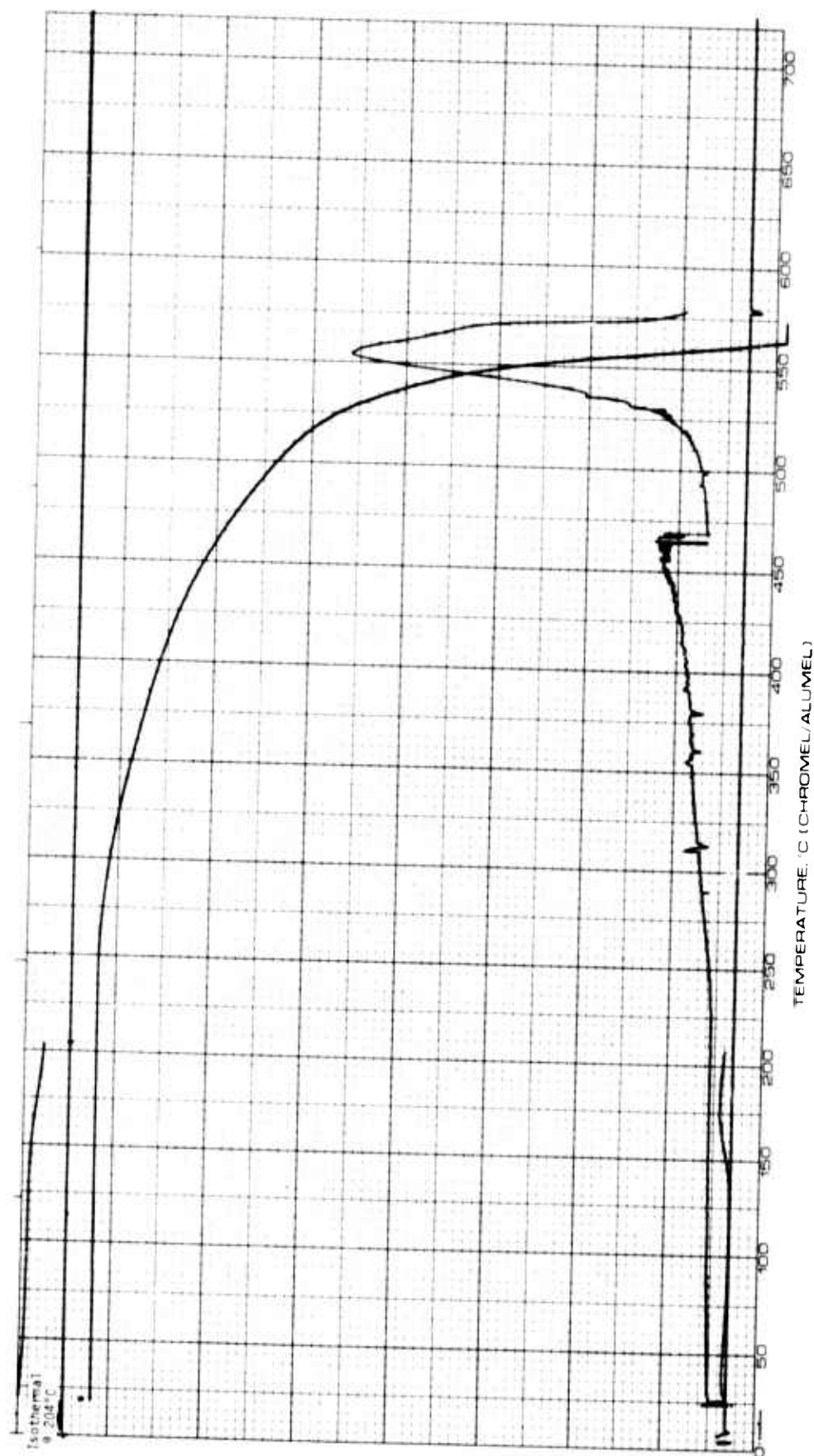


Figure 3. TGA Curve For Cured D01A Resin Prepared In Acetone

for 2.5 hours and then taken to decomposition. The results of this scan (see Figure 5) are the same as those obtained from the prepolymer prepared in methanol (see Figure 1). The cured sample, however, did not soften and coalesce as was observed for the DONA PMR resin prepared in methanol or acetone. It appears, therefore, that DMF aids in some fashion in the cure of the DONA resin.

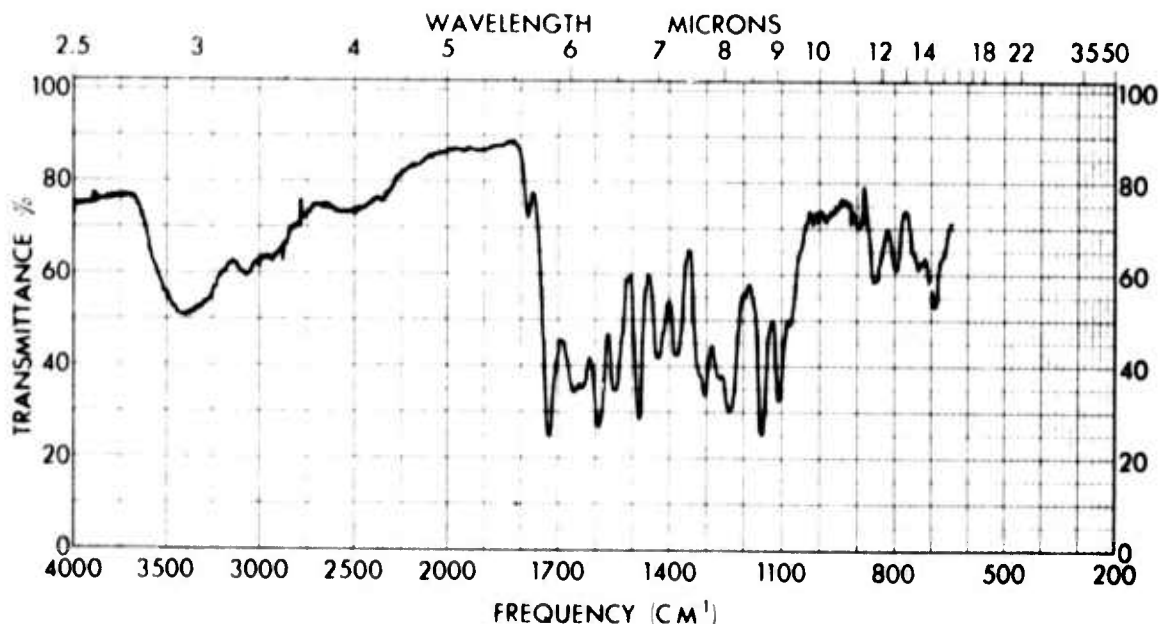


Figure 4. Infrared Spectrum (KBr) of DONA Prepolymer Prepared in DMF. Concentration: 3.1 mg/g KBr.

In an attempt to determine at which stage DMF influences the behavior of the DONA cure, a sample of the amide acid was isolated from the DMF varnish by precipitation. Specifically, a portion of the DMF varnish was added to ether and the resultant tacky solid then was dissolved in acetone and reprecipitated by adding the acetone solution to ether. The tacky solid was dried *in vacuo* at 176°F to give the light yellow DONA prepolymer. The infrared spectrum for this material is shown in Figure 6. The most obvious feature of the spectrum is a lower content of imide groups (carbonyl at 1780 cm^{-1}) in this prepolymer when compared to the prepolymer isolated by removing DMF *in vacuo* (see Figure 4).

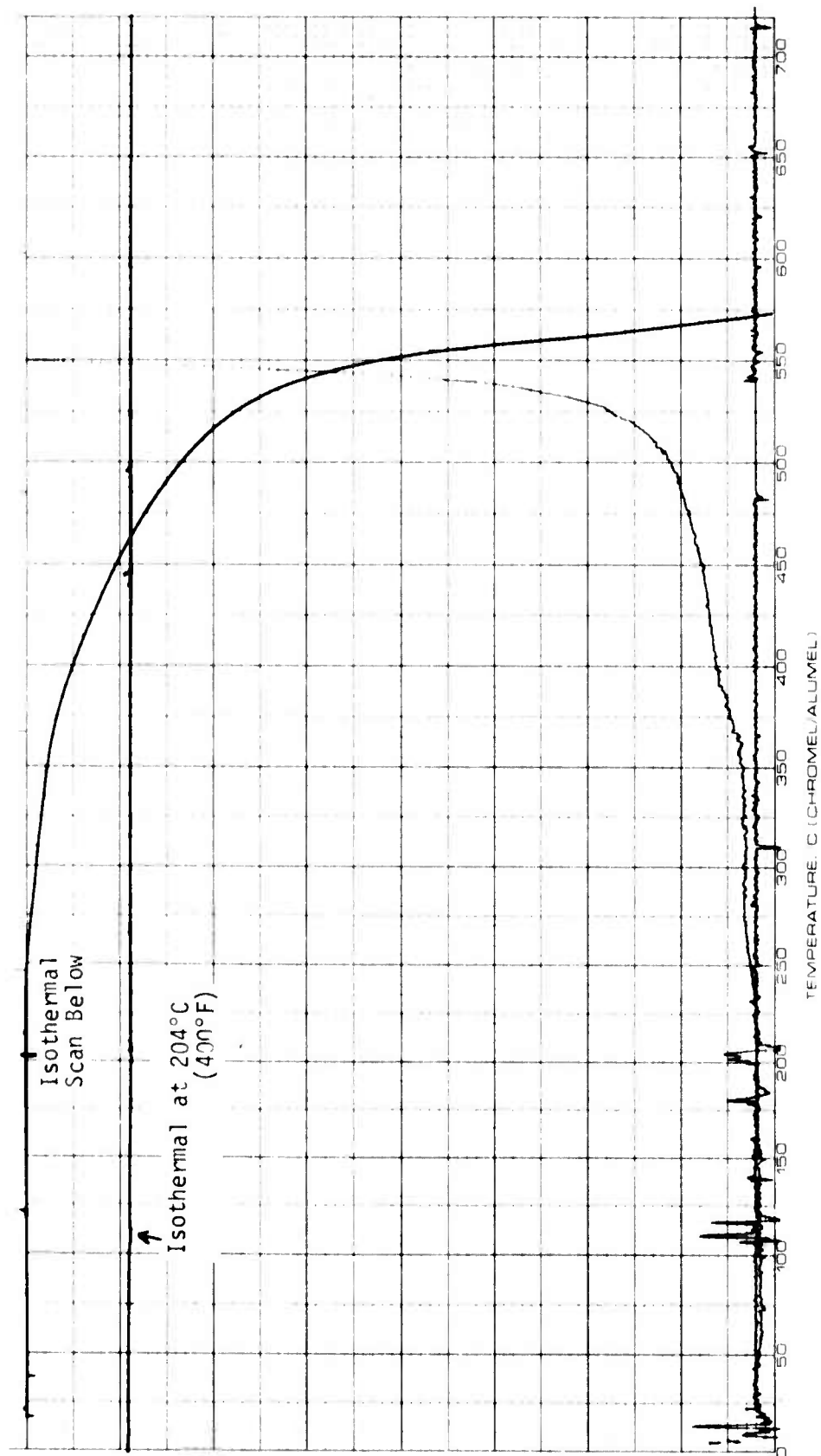


Figure 5. TGA Curve For Cured D0NA Resin (Prepolymer Prepared in DMF)

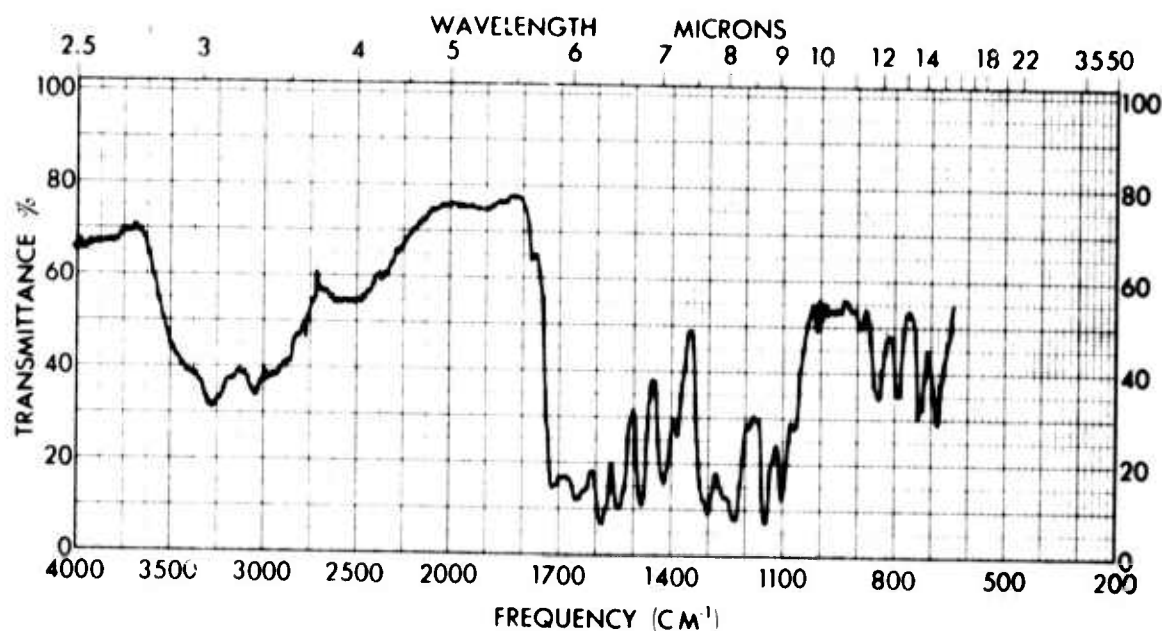


Figure 6. Infrared Spectrum (KBr) of DONA Prepolymer Prepared in DMF and Isolated by Precipitation. Concentration: 3.3 mg/g KBr.

A cured sample of the prepolymer displayed the same TGA results. The only significant difference between this cured sample and the cured sample derived from DMF was observed in the 450°F postcure treatment. This resin did soften slightly and partially coalesced. These results indicated that DMF promotes the imidization of the prepolymer at reaction temperatures below 400°F. This is very important because imidization of the prepolymer is required prior to resin gel to ensure that the DONA end-cap undergoes the expected cure chemistry.

Additional studies then were conducted to determine the structure of the compound obtained from 3,3'-sulfonyldianiline and the DONA end-cap, *i.e.*, in each solvent, methanol and DMF. The adduct was formed by treating the diamine with a stoichiometric amount of DONA end-cap (2 : 1 ratio) and then allowing the solvent to evaporate (simulating prepreg fabrication techniques). Samples of the resultant residue then were heated in an air circulating oven for two hours at the following temperatures; at 158°F, 240°F and 310°F.

Infrared analysis of the residues obtained from the above experimentation failed to show significant differences between the samples prepared in methanol and DMF. The infrared spectra for the samples prepared in DMF did contain a slightly more intense imide carboxyl bond (1760 cm^{-1}) as compared to the methanol derived samples. The imide band, however, was not as strong as would be expected, particularly for the sample heated at 310°F (see Figure 7). However, it is assumed that the residue DMF promotes imidization of the amide acid during cure.

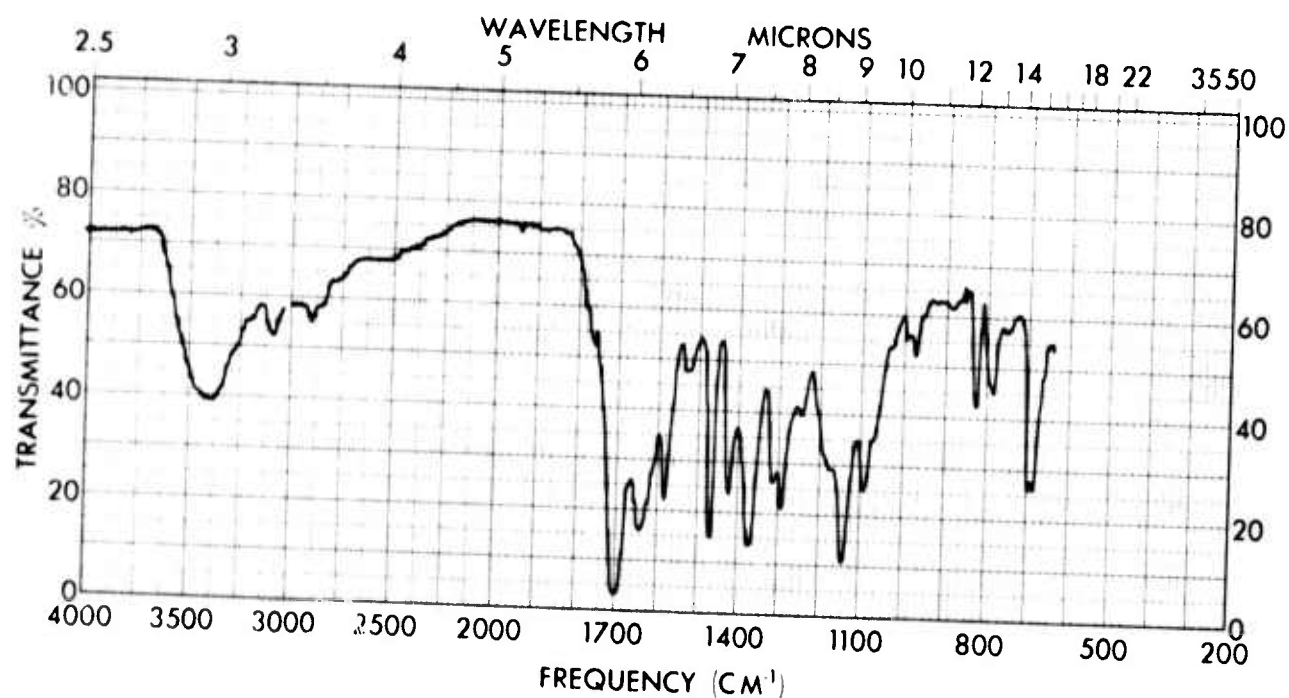


Figure 7. Infrared Spectrum (KBr) of 3,3'-Sulfonyldianiline/DONA Adduct Prepared In DMF. Heated at 310°F For 2 Hours. Concentration: 3.2 mg/g KBr.

Differential scanning calorimetric analysis of the samples prepared above showed that the methanol derived sample heated at 240°F displayed a number of endotherms in the temperature range of 356°F to 392°F (see Figure 8). There were no significant exotherms below 450°F . Conversely, the sample prepared in DMF displayed a fairly strong endotherm over the temperature range of 275°F to 374°F , followed by an exotherm (see Figure 9). It is important to note that the exotherm begins at $\sim 375^\circ\text{F}$. If cure is represented by the exotherm, it is obvious that DMF is promoting cure and

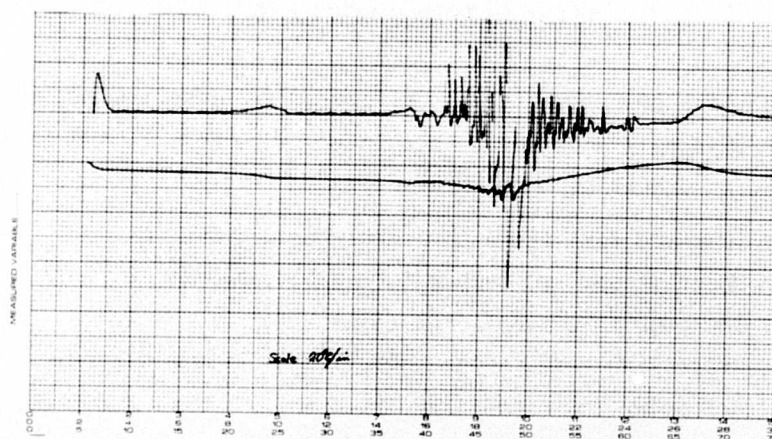


Figure 8. DSC Scan of 3,3'-Sulfonyldianiline/DONA Adduct (Prepared in MeOH) Heated at 240°F for 2 Hours.

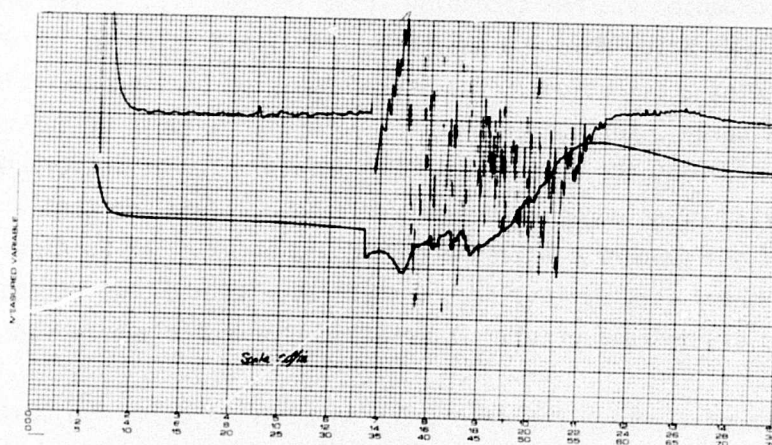


Figure 9. DSC Scan of 3,3'-Sulfonyldianiline/DONA Adduct (Prepared in DMF) Heated at 240°F for 2 Hours.

and that cure is occurring below 400°F which is the upper cure temperature. The sample derived from methanol, however, does not display an exotherm at 400°F; consequently, it is not expected to undergo complete cure. Therefore, it would appear that the DONA resin derived from methanol will not undergo cure below 400°F.

III. ADHESIVES DEVELOPMENT

The objective of Phase III was to develop new adhesive compounds based on the DONA polyimide resin selected during Phase II and to develop suitable bonding processes which provide:

- Improved resistance to hydrolytic degradation
- Moderate service temperature applicability
- Improved structural properties
- Processing ease, such as provided in state-of-the-art epoxy resin adhesive systems.

However, because of the unsatisfactory performance of the DONA polyimide resin produced via PMR technology (see Section II), it was decided to evaluate DONA amide acid and polyimide prepolymer solutions in DMF for adhesive bonding applications. The use of the high boiling DMF solvent was not considered a serious problem for adhesives because of the thin resin films and coatings used in adhesive joints. It was anticipated that thorough drying of an adhesive primer could be achieved and that a thoroughly dried glass scrim supported adhesive film could be used for bonding. Furthermore, preliminary work during Phase I (Reference 1) had demonstrated that there was no significant problem in removing DMF from glass fabric preregs.

The planned approach for developing an adhesive using the DONA polyimide resin was based on experience obtained under NASA Contract NAS 1-9532 (Reference 5). During the NASA program, it was demonstrated that the TRW A-type polyimide resins have poor adhesion to metal adherends. However, copolymer blends of the A-type polyimide with an amide-imide resin (Amoco AI-1137) provided high shear strength values at temperatures from -423°F up to +600°F (Reference 6). Consequently, the major thrust during Phase III was to develop similar copolymer blends for use in adhesive bonding of aluminum alloy substrates.

3.1 PRELIMINARY EVALUATION OF DONA/DMF RESIN

The initial phase of the adhesive screening effort consisted of obtaining base line data from which formulary variations could be compared.

This effort included the fabrication, machining and testing of two lap-shear panels made from 2024T3 clad aluminum alloy and aluminum filled DONA/DMF resin (see Table 8). Details of the adhesive and panel manufacture are provided below.

TABLE 8.
PRELIMINARY LAP-SHEAR STRENGTH FOR DONA/DMF VARNISH^{a)}

Test Temperature °F	Lap-Shear Strength, psi	Failure Mode
RT	2270	Adhesive
365	2320	Adhesive

a) Formulation: 12.0 g DONA resin solids
21.0 g Aluminum Powder
1.0 g Cab-O-Sil
18.0 g Dimethylformamide (DMF)

3.1.1 Adhesive and Adherend Preparation

Style 112 A1100 finished glass fabric was prepregged using an aluminum powder filled DONA/DMF paste (1.0 pbw resin solids to 1.75 pbw aluminum). The prepreg was air dried for 60 minutes, "B" staged 60 minutes at 150°F and 120 minutes at 250°F. Aluminum 2024T3 clad panels were cleaned using the FPL chromic acid etch and the cleaned faying surfaces primed with the same DONA/aluminum powder paste. The "B" staging cycle of the primed panels was the same as the adhesive tape.

3.1.2 Bonding Procedure

The primed faying surfaces then were mated, placed on an aluminum bonding fixture and inserted into a cold press. The assembly was heated to 400°F under 200 psi positive pressure and allowed to cure two hours. The assembly was cooled to ambient conditions, removed from the press and postcured 16 hours at 475°F.

3.2 PRELIMINARY EVALUATION OF DONA/AMIDE AMIDE COPOLYMER

The next panel fabricated utilized a DONA/amid imide (AI 1137) copolymer formulation, similar to P4/A5F (Reference 5). This consisted of blending the DONA amide acid solution in DMF with Amoco AI 1137 amide acid varnish at a calculated 50 : 50 ratio of resin solids. Aluminum powder was added to form an adhesive paste (1.0 pbw resin solids to 1.75 pbw aluminum). Panels were made using identical processing conditions as previously described (see Section 2.1), machined and tested (see Table 9).

TABLE 9.
PRELIMINARY LAP-SHEAR STRENGTH FOR DONA/AI 1137 COPOLYMER

Test Temperature °F	Lap-Shear Strength, psi	Failure Mode
RT	1960	Adhesive
365	1130	Adhesive

3.3 EVALUATION OF NA ADHESIVE FORMULARY AND PROCESSING CONDITIONS

Preliminary results of the DONA/AI 1137 copolymer (Section 3.2) indicated that the polyamide-imide did not enhance the lap-shear properties of the adhesive system. It was postulated that the processing conditions may have contributed to the low values, therefore a short formulary and processing screening matrix was performed. Processing conditions were the same as described in Section 3.2, except where specifically changed by the test matrix parameters. The only additional difference was the panels were cured in an autoclave (*i.e.*, vacuum bag pressure plus 100 psig). Panels were fabricated, machined and tested (see Table 10). As can readily be observed the only major processing factor to exhibit an effect on the adhesive panel properties was the "B" staging temperature. Because the properties (Table 10) were lower than the original control panel (Table 8), AI 1137 copolymer was not used in the next formulation and

another short process screening was performed (Table 11). This time the parameters studied were both the "B" staging conditions (time and temperature) and the postcure temperature. Processing remained the same except for the changes stipulated by the screening matrix. Again the lap-shear panels were autoclave molded using vacuum bag pressure plus 100 psig positive pressure. Panels after being processed then were machined and tested (see Table 11).

TABLE 10.
DONA/AI 1137 ADHESIVE SCREENING STUDY

Expt	Level of Factor				Lap-Shear Strength (psi)		
	A	B	C	D	RT	365°F	Failure Mode
1	-	-	+	+	1170	1280	Adhesive
2	-	+	-	-	1820	2500	Adhesive
3	+	-	-	+	1900	1840	Adhesive
4	+	+	+	-	1300	1170	Adhesive

A. Level of AI Filler
(Resin Solids : Filler)

1 : 1.25 1 : 1.75

B. Cure Time at 400°F

2 hours 4 hours

C. Drying Cycle

30 minutes/
150°F 60 minutes/
150°F

TABLE 11.
DONA ADHESIVE PROCESS SCREENING STUDY

Expt	Level of Factor ^{a)}		Lap-Shear Strength		
	A	B	RT(psi)	365°F(psi)	Failure Mode
1	-	-	870	880	Adhesive
2	-	+	1050	980	Adhesive
3	+	-	1460	1660	Adhesive
4	+	+	1370	1530	Adhesive

^{a)} A. Postcure Temperature

400°F 475°F

B. "B" Stage Conditions
Time/Temp.

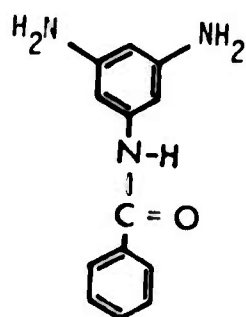
30'/150°F 60'/150°F
30'/250°F 60'/250°F

All of the room temperature shear strength values were lower than considered acceptable for a structural adhesive, *i.e.*, <3000 psi. However, the values at 365°F test temperature all were equal to or higher than the room temperature values. It was hypothesized that the low values at room temperature could be attributed to resin brittleness and, because the resin at 365°F is probably less brittle due to thermoplasticity, this would explain the high relative values at 365°F. Consequently, double lap-shear test panels were prepared in order to evaluate the DONA adhesive when minimal peel loading is applied during test. The results of this study did not confirm the resin brittleness hypothesis (see Table 12). Values obtained during this study were similar to the single lap-shear test values and all failures were adhesive. Consequently, it was concluded that the DONA polyimide resin is not suitable for use in adhesive compounds. Also, because the DONA cure occurs at a lower temperature than condensation cure amide-imide resins, *e.g.*, Amoco AI 1137, copolymer blends are not compatible. However, it is feasible that a DONA amide-imide resin could provide satisfactory adhesive characteristics if prepared as an amide-acid in DMF solution. Use of DMF probably would not be a problem when used as a solvent in adhesive formulations.

TABLE 12.
DOUBLE LAP-SHEAR TESTS

Test Temperature, °F	Lap-Shear Strength, Psi
R.T.	1710
365	1800

One approach considered was to use new ingredients such as the mono-benzamide of 1,3,5-triaminobenzene (see structure below), which when employed as an aromatic diamine in conjunction with BSDA, would in effect give a stable aromatic backbone possessing aromatic amide groups to enhance the adhesive properties of the resin. However, to develop a DONA amide-



imide resin would require considerable basic polymer development work beyond the planned scope of this program.

APPENDIX A.

RESIN PREPARATION

I.1 PREPARATION OF DONA LAMINATING VARNISH IN METHYL CELLOSOLVE

To a solution of 69.3g (0.35 mole) of methylene dianiline in 500g of methyl cellosolve, 67.9g (0.35 mole) of finely powdered DONA was added slowly while cooling the mixture in an ice bath. The mixture was stirred an additional 20 minutes after a clear solution was obtained, and then 94.94g (0.175 mole) of BSDA was added over a 15-minute period. The last traces of BSDA were washed into the reaction flask with an additional 196g of methyl cellosolve (696g total solvent) and the mixture was stirred for 1 hour with cooling. The varnish was stirred an additional 30 minutes after a clear solution was obtained before being used in prepreg manufacture.

I.2 PREPARATION OF DONA PMR VARNISH

The preparation of BSDA and the corresponding dimethyl ester have been described previously (References 1 and 2). Preparation of a varnish is described below.

To a stirred solution of 24.8g (0.10 mole) of 3,3'-sulfonyldianiline in 35g of methanol was added 19.8g (0.10 mole) of DONA under a nitrogen atmosphere. The reaction mixture was cooled with an ice-bath during the preparation of the varnish. The mixture was stirred for twenty minutes after the DONA was added until a clear solution was obtained. To this solution was added portionwise 30.3g (0.05 mole) of BSDA dimethyl ester. The last traces of the ester were washed into the flask with an additional 65g of methanol. The varnish was maintained under a nitrogen blanket prior to use.

APPENDIX B.

TEST PROCEDURES FOR CHARACTERIZATION OF PREPREG AND COMPOSITES

II.1 RESIN CONTENT BY BURN-OFF

Samples of cured glass fabric reinforced composite or prepreg were weighed in a tarred crucible and then placed into an 1050°F muffle furnace. After constant weight was attained (usually after one hour for prepreg and four hours for composite) the resin content was calculated:

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

Where:

W_r = Weight content of resin solids, %

W_1 = Weight of original sample, g

W_2 = Weight of specimen after burn-off, g

II.2 RESIN CONTENT BY ACID DIGESTION

The resin was digested from cured graphite fiber reinforced samples by pouring concentrated sulfuric acid (120 ml) onto the sample in a glass beaker and then heating the acid for a minimum of 20 minutes 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 350°F air circulating oven. Resin solids contents were calculated:

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

Where:

W_r = Weight content of resin solids, % w/w

W_1 = Weight of cured composite sample, g

W_2 = Weight of filaments after acid digestion of the
resin matrix, g

II.3 VOLATILE MATTER CONTENT

Volatile matter contents were determined by weight loss after exposure of a 0.5 g prepreg sample in an air circulating oven at 400°F for 30 minutes.

II.4 DENSITY OF COMPOSITES

Density of composites was determined from measured volumes (air pycnometer) and weights of specimens.

II.5 COMPOSITE FIBER VOLUME

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

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

Where:

V_f = Volume percent fiber, ml

D_c = Measured density of composite, g/ml

D_f = Density of fiber, g/ml

K = Weight fraction, resin

The specific gravity of the Courtaulds A-S fiber is 1.80 g/ml and of the cured P10P polyimide resin is 1.33 g/ml.

II.6 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/ml

D_r = Density of resin, g/ml

D_f = Density of fiber, g/ml

W_r = Weight content of resin, percent

W_f = Weight content of fiber, percent

II.7 PERCENT RESIN FLOW OF PREPREGS

Percent resin flow was determined by weight loss determinations on molded prepreg flow specimens (six-ply prepreg, 45° bias, 4-inch by 4-inch square) after removal of the resin flash.

Flow properties were calculated:

$$F_w = \frac{W_1 - W_3}{W_1} 100$$

and

$$F_d = \frac{W_2 - W_3}{W_2} 100$$

Where:

F_w = Percent wet resin flow, % w/w

F_d = Percent dry resin flow, % w/w

W_1 = Initial weight of prepreg specimen, g

W_2 = Weight of prepreg sample after molding, g

W_3 = Weight of prepreg sample after molding and with resin flash removed, g

II.8 SHEAR STRENGTH OF COMPOSITES

The cured composites were machined into short beam shear specimens 0.25-inch wide by 6t long and tested in flexure at a mid-span loading point using a 4:1 span to depth ratio. Loading rate was 0.05-inch/minute.

Shear strengths were calculated using the simple formula:

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

Where:

S_u = Ultimate shear strength, psi

V = Load at failure, lb

t = Specimen thickness, inch

b = Specimen width, inch

11.9 FLEXURAL PROPERTIES OF COMPOSITES

The cured composites were machined into flexural specimens 0.5-inch wide by 5-inch long and tested in flexure using a two-point loading and a 32:1 span-to-depth ratio. Loading rate was 0.05-inch/minute.

Flexural strengths and moduli were calculated using the formulae:

$$F_u = \frac{3 PL}{4bd^2}$$

and

$$E_b = \frac{L_m^3}{bd^3} \times \frac{11}{64}$$

Where:

F_u = Stress in the outer fiber at mid-span, psi

E_b = Modulus of elasticity in bending, psi

P = Load at failure, lb

L = Span, inch

b = Width of specimen, inch

d = Thickness of specimen, inch

m = Slope of the tangent to the initial straightline portion of the load deflection curve, lb/inch

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