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AFML-TR-73-243
VOLUME II

EXPLORATORY DEVELOPMENT OF PROCESSABLE LAMINATING RESINS WITH IMPROVED TOUGHNESS AND MODERATE TEMPERATURE CAPABILITY

PHASE II AND III

TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

TECHNICAL REPORT AFML-TR-73-243, VOL. II
JULY 1974

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

NOTICE

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

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Project Monitor

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Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Further studies were performed with the hydrolytically stable DONA polyimide resin developed under Phase I of this program. Objectives of the Phase II and III studies were to identify a DONA resin formulation that does not contain TDA, to identify a lower boiling solvent system than DMF or NMP, to identify an alternative low temperature curing end-cap to DONA, and to evaluate DONA and DAS resins as adhesives. It was demonstrated that TDA is not an essential constituent of the autoclave moldable DONA polyimide resins containing BSDA. However, attempts to identify a lower boiling solvent or an alternative end-cap to DONA were unsuccessful. Adhesive bonding studies demonstrated high promise for the DONA resin system as a structural adhesive. These studies indicated low promise for the DAS resins as structural adhesives.

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. Additional participants were Dr. R. J. Jones, Mr. M. K. O'Rell, Mr. C. H. Sheppard, Mr. K. K. Ueda and Dr. G. Zakrzewski. TRW Systems program administrative and review personnel were Dr. E. A. Burns, Mr. B. Dubrow and Mr. R. Hammel.

The report covers the period from 1 June 1973 through 1 June 1974.

A previous report AFML-TR-73-243 (Phase I) covers the period from 1 June 1972 through 1 June 1973.

The Contractor's report number is 22298-6026-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, WPAFB, Ohio, USAF under Phase II and III of Contract F33615-72-C-2122 during the period 1 June 1973 through 31 May 1974. The objective of this program is 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 work reported herein is a continuation of the Phase I activities (Reference 1). During Phase I, two novel polyimide resin systems were developed and evaluated that were designed to provide:

- High humidity resistance and low diffusivity to moisture at R.T. and elevated temperature
- Thermo-oxidative stability to 365°F
- Toughness and resistance to embrittlement at -65°F to 75°F
- Low to zero creep over the full range of use temperatures (-65°F to 365°F)
- High mechanical properties and continuous property retention at maximum use temperatures
- Final cure by a mechanism that does not evolve gases to provide low void content (maximum 2% v/v) composite structures
- Facile processability and cure enabling autoclave hardware fabrication at reasonable conditions (*e.g.*, up to 400°F cure at 100-150 psi for <4 hours)

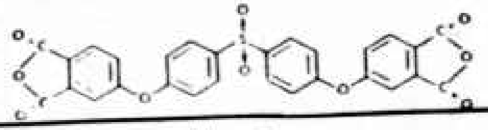
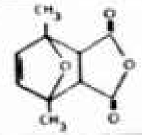
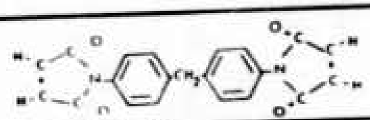
These two polyimide resin systems, termed as DAS and DONA polyimide resins throughout this report are described briefly as follows:

- DAS Polyimide Resins - These are linear polyimide polymers which contain 4,4'-diaminostilbene (DAS) as a backbone constituent. Crosslinking through residual unsaturation provided by the DAS constituent in the linear polyimide prepolymer is induced by a peroxide compound at temperatures ∿400°F. A poly-aliphatic ether diamine is used as a constituent in these resins to impart flexibility (toughness).
- DONA Polyimide Resins - These are TRW A-type polyimide resins (similar to P105A developed under Contract F33615-70-C-1392) but with 3,6-dimethyl-3,6-endooxy-1,2,3,6-tetrahydrophthalic anhydride (DONA) end-caps which cure ∿400°F. The specific formulation selected during Phase I consisted of a 1200 formulated molecular weight polyimide prepolymer of DONA/80MDA:20TDA/BSDA (see Table I).

The Phase I work demonstrated that the DONA polyimide resin could meet the program objectives for a laminating resin. The DAS resin demonstrated high promise but it also was clear that considerable resin formulary studies would be necessary in order to obtain a satisfactory DAS laminating resin. Work performed with the DONA resin provided graphite fiber reinforced composites that do not undergo the same drastic elevated temperature mechanical property degradation after exposure to humid atmosphere as the currently available high performance epoxy resin systems. Processability of the DONA resin was equivalent to the epoxy resins, *i.e.*, cure temperature <400°F and molding pressure <100 psig. Mechanical properties and elevated temperature (*i.e.*, 365°F) strength retention were shown to be equivalent to the high performance epoxy resin systems. Fracture toughness values of the new polyimide resin were lower than those obtained with the epoxy resin. However, the fracture toughness values obtained during Phase I were not considered to be representative of the resin system when processed under optimum conditions.

TABLE I.
KEY CONSTITUENTS OF CANDIDATE POLYIMIDE RESINS

KEY CONSTITUENTS OF CANDIDATE POLYIMIDE RESINS

Name of Constituent	Abbreviation	Structure	Attribute
bis(3,4-Dicarboxy-phenoxyphenyl) sulfone dianhydride	BSDA		Provides low temperature melt and flow to both linear and end capped polyimide prepolymers.
3,6-Dimethyl-3,6-endooxy-1,2,3,6-tetrahydrophthalic anhydride	DONA		Low temperature curing end cap for addition polymerization of polyimide prepolymers.
4,4'-Diaminostilbene	DAS		Provides facile cure by peroxide methodology.
bis(4-Maleimido-phenyl) methane	BMPM		Crosslinks with DAS in linear polyimides.
Methylene Dianiline	MDA		Contributes high processability, particularly in combination with TDA.
Thiodianiline	TDA		Contributes melt and flow characteristics in combination with other aromatic diamines; key ingredient in P105A resin developed in Contract F33615-70-C-1352.
Polyaliphatic Ether Diamines	PED	$H_2NCH_2CH_2O(CH_2CH_2O)_x CH_2CH_2NH_2$ a)	Long chain segment to accomplish the same objective as HMD.
Hexamethylene Diamine	HMD	$H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$	Short aliphatic chain segment to lower polymer melt/flow temperature and to provide flexibility/toughness.

a)Repeat unit x-8, 13 and 15 to yield reactants of molecular weight of 400, 600 and 700, respectively.

Phase II Composites Studies discussed in this report were concerned primarily with modification of the DONA resin in order to provide a viable system suitable for use in manufacturing facilities. These modifications were necessary in order to meet two key requirements:

- During Phase I, TDA was used in the resin formulation to induce resin flow. This material became unavailable commercially at the end of Phase I activities. Consequently, it was necessary to formulate a DONA resin that did not contain TDA.
- Two solvent systems were used during Phase I, *i.e.*, DMF and NMP. These solvents both are high boiling making them difficult to process during prepreg preparation and difficult to remove completely during composite molding. Consequently, it was necessary to identify an improved low boiling solvent system.

As described in the text of this report, a satisfactory resin system was developed which did not contain TDA. However, attempts to identify a lower boiling solvent than DMF or NMP were unsuccessful. Consequently, Phase II work will be continued during the next twelve months using DONA resin in DMF solutions with the objectives of optimizing resin processability, obtaining higher fracture toughness values and manufacturing large pseudo-isotropic panels without micro-cracks.

Phase III Adhesives Studies performed during this twelve-month period were concerned with the evaluation of the DAS and DONA resins for structural adhesive bonding applications. The DONA resin was selected for this application and consequently, will be optimized as an adhesive resin during the next twelve-month period. After a satisfactory DONA adhesive resin has been identified, adhesive compounding studies will be performed.

The Phase II and III activities are divided into tasks as follows:

- PHASE II - COMPOSITES STUDIES
  - TASK I - RESIN OPTIMIZATION
  - TASK II - PROCESS DEVELOPMENT AND COMPOSITE EVALUATION
  - TASK III - RESIN MANUFACTURE
  - TASK IV - FABRICATION AND TESTING STRUCTURAL PANELS
- PHASE III - ADHESIVE STUDIES
  - TASK I - ADHESIVE EVALUATION
  - TASK II - ADHESIVE RESIN OPTIMIZATION
  - TASK III - DEVELOPMENT OF ADHESIVE SYSTEMS

This report describes work performed in Phase II, Tasks I, II and III and Phase III, Task I during this twelve-month report period; work will continue on these tasks during the next twelve-month period. The report is divided into sections covering the Composites Studies and Adhesives Studies. The significant conclusions reached and assessments of the results are listed as well as Appendices covering detailed descriptions of procedures used in material preparation, composite processing and testing.

II. PHASE II COMPOSITES STUDIES

The first objective of Phase II was to develop a DONA polyimide resin that meets the program's processing and performance requirements but which does not contain thiodianiline (TDA). This diamine originally was used in the DONA polyimide resin formulation developed during Phase I (Reference 1) to induce resin flow. In Phase II work, it was necessary to replace TDA because this material was withdrawn from the market due to suspect carcinogenic character.

The second and equally critical objective of the Phase II Composites Studies was to develop a DONA polyimide laminating varnish containing an improved solvent system over the NMP and DMF solvents used previously (Reference 1). Key improvements sought from the improved solvent system were:

- Lower boiling point to provide rapid and complete removal of the solvent system prior to resin cure and hence give improved 365°F retention of composite properties, and
- Lower toxicity of the improved solvent system than DMF or NMP.

Two approaches were investigated during Phase II 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 2) to the DONA resin.

Simultaneous processing studies were performed using the DONA resin modifications in order to obtain an expedient evaluation with A-S graphite fiber reinforcement. These studies included development of both prepreg preparation and autoclave molding processes. Also, work was performed on the installation and check-out of a scale-up facility intended for ultimate larger scale production of BSDA and resin in continuing program activities.

The Phase II work was performed in three tasks:

- TASK I - RESIN OPTIMIZATION
- TASK II - PROCESS DEVELOPMENT AND COMPOSITE EVALUATION
- TASK III - PRELIMINARY INGREDIENT AND RESIN SCALE-UP PRODUCTION

2.1 TASK I - RESIN OPTIMIZATION

An immediate concern with the DONA resin system identified during Phase I of this program [*i.e.*, DONA/80MDA:20TDA/BSDA (1200 FMW), Reference 1] had to be resolved in Phase II studies. This was related to the termination of commercial production of thiodianiline (TDA). Originally, this diamine (TDA) was used to induce resin flow with P105A resin developed under Contract F33615-70-C-1392 (Reference 3). The TDA was removed from the market because vendor studies had shown that this diamine is suspect as a carcinogen. Therefore, it became necessary to identify an alternative DONA polyimide resin formulation to the TDA containing system. This was accomplished prior to initiating solvent studies as discussed in Section 2.1.1.

It also was identified, during Phase I of this program (Reference 1), that an improved solvent system was required in order to optimize the properties of DONA/A-S graphite fiber composites. Apparently, incomplete removal of the last traces of residual solvent caused either high voids or poor elevated temperature property retention of the resultant composites.

Work was conducted to explore the possibility of formulating a low boiling point azeotrope of NMP which would result in complete solvent removal. The desired azeotropes were not identified but several co-solvents containing NMP were evaluated. Studies showed that this approach was not satisfactory because apparently residual traces of NMP remained in the resin matrix of cured panels (characterized by low strength retention at 365°F) as was observed in Phase I for the NMP mono-solvent system. Consequently, another approach for providing varnishes using low boiling point solvents was explored. This approach was a modification of the polymerization of monomeric reactants (PMR) technology developed at NASA Lewis Research Center (Reference 2). This work is described in Sections 2.1.2 and 2.1.3.

2.1.1 Evaluation of Alternative Non-TDA Containing Resin Formulations

It was necessary to identify alternative resin formulations to the 1200 FMW DONA/80MDA:20TDA/BSDA used throughout Phase I because of the suspect carcinogenic character of TDA. Although several alternative diamines to TDA were considered, the most logical initial approach was to identify whether a codiamine system was required for use with MDA in order to attain the desired resin flow properties during the autoclave melt/consolidation/cure cycle.

Glass fabric prepreg was prepared containing Style 181 E-glass, I-545 finish and the Phase I DONA resin formulation (*i.e.*, 1200 FMW DONA/80MDA:20TDA/BSDA). Similar prepreg was prepared using a DONA resin formulation without TDA (*i.e.*, 1200 FMW DONA/MDA/BSDA) prepared by the normal procedure (see Appendix I). Laminates then were autoclave molded simultaneously in the same vacuum bag from both batches of prepreg using the Phase I process (see Appendix II).

The resultant laminates both appeared to be well consolidated and both demonstrated excellent resin flow. Evaluation of the laminates showed that both suffered from low resin content (∿23% w/w) resulting from excess resin flow. However, the measured mechanical properties (see Table II) demonstrated that both resins provided equivalent properties. A small A-S graphite fiber composite containing the 1200 FMW DONA/MDA/BSDA resin was autoclave molded by the same process because of the apparent identical behavior of the two resins on E-glass. This laminate also was well consolidated and provided a flexural strength of ∿200 Ksi.

It was concluded from these results that the DONA end-capped polyimide resin does not require TDA in the formulation in order to obtain autoclave moldability as is most definitely the case if the dianhydride employed is benzophenone tetrocarboxylic acid dianhydride (BTDA) (Reference 3). Consequently, the DONA/MDA/BSDA formulation was employed for the remainder of Phase II studies.

TABLE II.

PRELIMINARY EVALUATION OF DONA RESINS WITH AND WITHOUT TDA[a)]

Property	DONA Resin Formulation	
	With TDA[b)]	No TDA[c)]
Flexural Strength, Ksi		
at R. T.	134	140
Standard Deviation	3.5	6.8
at 365°F	99	97
Standard Deviation	1.1	1.2
Strength Retention, %	74	69
Resin Content, % w/w	23.2	22.7

[a)] Using autoclave molded, Style 181 E glass fabric laminates.

[b)] DONA/80 MDA:20TDA/BSDA (1200 FMW)

[c)] DONA/MDA/BSDA (1200 FMW)

2.1.2 Development of Improved Solvent System for DONA Polyimide Resin

The successful demonstration of a suitable non-TDA containing resin enabled studies to be initiated early in Phase II work to identify a more suitable solvent system than the NMP mono-solvent system.

Experimental work was performed to explore the possibility of formulating a low boiling point azeotrope of NMP that would provide:

- High solids content resin solutions (∿30-40% w/w)
- Rapid solvent removal during prepreg drying
- Complete solvent removal during the autoclave molding cycle

A total of six co-solvents were selected for this study. These co-solvents all are relatively low boiling and are representative of five different classes of available and commonly used organic compounds.

The co-solvents screened for use in formulating a low boiling azeotrope of NMP are given in Table III. During this study, 60/40 (v/v) mixtures of NMP and the respective co-solvent component were prepared and distilled at atmospheric pressure through a straight distillation head. The boiling point and volume of the distillates were recorded during the process. For all solvents studied, it was found that the co-solvent component was simply removed by distillation from the NMP. No azeotrope formation was observed for any of the mixtures employed in the investigation.

TABLE III.
CO-SOLVENTS SCREENED

	Boiling Point (°F)	Solvent Class
Xylene	280	Aromatic hydrocarbon
Methyl ethyl ketone	176	Ketone
Ethyl acetate	171	Ester
Tetrahydrofuran	151	Ether
Ethanol	172	Alcohol
Isopropanol	180	Alcohol

Additional laboratory work was conducted to test the feasibility of use of the solvent mixtures given in Table III to permit rapid removal of the lower boiling solvent during prepreg manufacture because true azeotrope mixtures were not achieved. The two lower boiling solvent candidates selected for study were acetone and tetrahydrofuran (THF). The original 60/40 (v/v) mixture of selected co-solvent components and NMP was varied and DONA resin was added to give a 40% w/w solids loading. The solutions obtained were stored in closed containers and checked periodically for evidence of precipitation.

It was found that a 40% w/w resins solid loading could be obtained in a mixture of 80/20 (v/v) acetone/NMP wherein the resin remained in solution for 7 days before precipitation was noted. A 50% w/w solids loading was obtained in a 70/30 (v/v) acetone/NMP mixture and the resin remained in solution for one month. The 80/20 (v/v) mixture was found to be the lowest level to which NMP could be diluted with acetone before immediate or short-term precipitation occurred at 40% w/w solids. It was established also that high dilution technique (20% w/w solids loading) would not give a suitable varnish at a 85/15 (v/v) acetone/NMP mixture.

Tetrahydrofuran (THF) also showed promise as a co-solvent candidate. A 50% w/w solids solution was prepared in 70/30 (v/v) THF/NMP. No resin precipitation occurred during a 21-day test period.

A preliminary composite evaluation of the acetone/NMP and THF/NMP co-solvent varnishes showed that although the desired rapid removal of the volatile component was achieved, traces of NMP again remained in the structure and unsuitable properties resulted. Because of the failure of dilution methodology to render NMP as a suitable fabrication solvent, further work on aprotic solvents was terminated and an alternative approach was investigated as described in Section 2.1.3.

2.1.3 Screening of a PMR Approach

The results obtained during Phase I (Reference 1) employing NMP and DMF as laminating solvents indicated that solvent selection is key to obtaining the desired mechanical properties for composites. For example, an improvement in shear strength was observed for the composites when NMP was used in place of DMF. However, use of NMP as a solvent or co-solvent component (see Section 2.1.2) made it more difficult to process the composites in order to obtain acceptable elevated temperature strength retention values.

A feasible approach to circumvent the use of DMF and NMP as solvents was the polymerization of monomeric reactants (PMR) developed at NASA Lewis Research Center (Reference 2). In this approach, a combination of esters and amines in methanol solvent is used as a laminating varnish at a stoichiometry level to yield a given formulated molecular weight (FMW) prepolymer. Because methanol is a low boiling point solvent which would be easy to remove during autoclave molding, this approach was investigated.

As the first step in this evaluation, experimental work was conducted to prepare the monomers required for the PMR approach. The dimethyl ester of BSDA was prepared by refluxing the dianhydride in methanol which provided a dimethyl ester with a high (50% w/w) solubility in methanol. Problems were encountered in the preparation of a desired DONA monomethyl ester because conventional esterification procedures yielded undesirable side products (see Section 2.1.4.2). For this reason, the standard PMR formulary (Reference 2) had to be modified. This was accomplished by employing a two-ingredient PMR approach.

The use of DONA-MDA amide-acid, as prepared by reacting equal molar stoichiometric amounts of DONA and MDA in methanol, was studied as an alternative to DONA monomethyl ester and MDA. It was observed that a varnish could be obtained by preparation of the DONA-MDA amide-acid in methanol followed by the addition of the BSDA dimethyl ester in an amount yielding a 30% w/w ingredients solids loading. A varnish of this formularly prepared at 35-40°F was stable for 5 hours at this temperature. The use of simple solvents similar to methanol (*e.g.*, acetone, MEK, and IPA) did not increase varnish shelf life. Because the five-hour varnish stability provided sufficient time for prepreg fabrication, the DONA-MDA amide acid/BSDA dimethyl ester ingredients in methanol were employed to prepare A-S graphite fiber reinforced composites. A composite was fabricated using the cure cycle identified earlier for the DONA/MDA/BSDA prepolymers. The resultant composite properties were promising (see Section 2.2) although the need for additional resin studies also was identified. Consequently, additional detailed PMR resin preparation studies were performed (see Section 2.1.4).

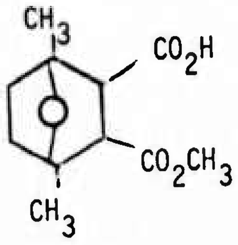
2.1.4 Detailed PMR Studies

The results of the preliminary processing studies on the PMR approach indicated high promise and also identified problem areas to be solved. In the latter cases, the use of the DONA-MDA amide-acid instead of the desired monoester of DONA provided a laminating varnish of relatively short shelf-life (see Section 2.1.3). Also, it has been reported recently that the purity of the other ester monomer, the diester of the dianhydride (BSDA), greatly influences the properties of the final composite (Reference 3). Therefore, the following studies were conducted to identify an optimized resin formulation:

- Development of a reproducible synthesis method for preparing the dimethylester of BSDA

- Investigation of a suitable synthesis method for preparing the monomethyl ester of DONA
- Definition of the shelf-stability of methanol varnish as prepared from higher quality ingredients.

The desired methyl ester structures are shown below for DONA and BSDA. The results from synthesis studies utilizing various methods are presented in Sections 2.1.4.1 (BSDA) and 2.1.4.2 (DONA). Section 2.1.4.3 discusses the aging studies on the resin varnish prepared from a DONA derivative and the dimethyl ester of BSDA.



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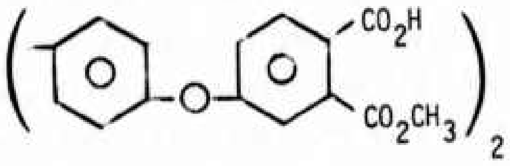


II

2.1.4.1 Synthesis Studies to Yield Reproducible Dimethyl Ester of BSDA - Initial preparations of *bis*(3,4-dicarboxyphenoxyphenyl)sulfone dimethyl ester (Compound II) have yielded products of indeterminate and unreproducible purity. The first procedure employed was a simple reflux of BSDA and methanol for six hours at which time the original white suspension became a clear solution. It was presumed that formation of a clear solution indicated conversion of the two anhydride groups in BSDA, which is insoluble in methanol, had been completed. However, product analysis by NMR exhibited a methyl proton to aromatic proton number ratio significantly less than the theoretical ratio of 0.43:1.0.

Consequently, longer reaction times of up to ∿48 hours were investigated (details are given in Appendix I). During these studies, the original white suspension again became clear after six hours. However, the additional reflux duration produced a product that possessed a methyl to aromatic proton ratio nearer to the theoretical number. Apparently an equilibrium mixture of compounds containing different numbers of methyl groups (*i.e.*, 1-4) is achieved during this period and greater reaction times have no effect on the composition of the mixture. Repeated experiments yielded reproducible mixtures which gave reasonable composite properties (see Section 2.2.2).

An alternative synthesis procedure was evaluated using sodium methoxide as the methylating agent to produce the desired ester. The reaction was run both as a suspension in benzene and a solution in methanol. The product obtained from the reaction conducted in methanol gave a proton NMR spectrum very similar to the material obtained without the sodium methoxide (see above). Because the sodium methoxide reaction resulted in apparently the same product as simple reflux in methanol and the latter is more cost effective, further experimentation with methoxide was terminated.

2.1.4.2 Further Attempted Synthesis of Monomethyl Ester of DONA - Previous efforts to prepare the desired monomethyl ester of DONA by simple refluxing in excess methanol resulted in reverse Diels-Alder decomposition of the bicyclic compound yielding 2,5-dimethylfuran and dimethyl fumarate, as indicated by proton NMR spectroscopy. Consequently, sodium methoxide was used as the methylating agent based on the assumption that because methoxide is more nucleophilic than methanol, it would allow the use of lower reaction temperatures (*i.e.*, <R.T.) and thus minimize the reverse Diels-Alder decomposition.

When the reaction was conducted at room temperature (in a manner similar to the reaction given in detail in Appendix I) a solution was obtained. On acidification with aqueous hydrochloric acid, a mixture of products was indicated by NMR in which dimethyl fumarate predominated.

Similar reactions conducted at 32°F in methanol resulted in a white crystalline solid, presumably the monomethyl ester-monosodium salt of DONA. Although this material appeared to be stable at room temperature, when exposed to ambient atmosphere, it quickly liquified (with no discoloration) probably due to a very hygroscopic character of the salt. Acidification of a methanol solution of this solid with dry hydrogen chloride at 32°F resulted in the precipitation of sodium chloride. Removal of the methanol solvent from the colorless mother liquor resulted in a green liquid which darkened in a period of several hours. NMR spectroscopy of this green colored material showed that decomposition of the bicyclic system had occurred yielding methyl fumarate.

As a result of the unsuccessful direct methanol esterification attempts, as well as the sodium methoxide conversions, no further work to synthesize the desired material was conducted. Because of these observations and other unsuccessful attempts at DONA ester preparation by direct addition of dimethylfuran to a maleic ester (Reference 1), it was concluded that the mono- and/or dimethyl ester of dimethyloxynadic acid is unstable at room temperature.

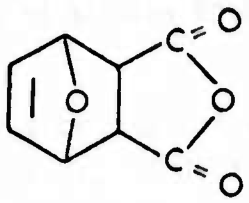
2.1.4.3 Resin Varnish Aging Studies - A 30% by weight solution of BSDA dimethyl ester and the amide-acid of methylene dianiline (MDA) and DONA in methanol was prepared. Samples were withdrawn and were diluted to 25% and 20% by weight, respectively. These samples of each concentration were stored under nitrogen for varnish aging assessment.

The 30% w/w solution formed large amounts of precipitate in ∿24 hours. This precipitate was filtered and dried at 140°F in a vacuum oven. The product did not display a melting point and was identified to be primarily an amide-acid by infrared analysis.

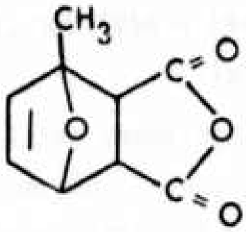
The 20% and 25% w/w samples each produced small amounts of precipitate after 2 hours which increased up to 24 hours. After this point in time, no additional precipitate formed on standing for 144 hours. These results show that additional solvent studies must be conducted before a shelf-stable resin varnish is identified.

2.1.5 Evaluation of Alternative End-Caps

Early in Phase II work, screening studies were conducted to investigate the utility of end-caps of a similar structure to dimethyl oxynadic anhydride (DONA) used in the most promising resin selected during Phase I. Specifically, oxynadic anhydride (ONA) and 1-methyl oxynadic anhydride (MONA) were selected for this study as potentially low cost or easier processable homologs of DONA.



ONA



MONA

The ONA and MONA compounds were prepared from the appropriate furan and maleic anhydride in high yield (>90%) *via* a Diels-Alder condensation. The structure of each compound was confirmed by infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) and melting point. A representative experimental procedure, together with spectra, are given in Appendix I.

These end-caps were used subsequently to prepare prepolymers using a similar stoichiometry formulation as that used for the most promising DONA prepolymer identified in Phase I [*i.e.*, DONA/80MDA:20TDA/BSDA (1200 FMW)]. This formulary (*i.e.*, TDA was used) was employed in order to compare the results with the detailed evaluation data determined in Phase I (Reference 1). If successful, it was intended to use the alternative end-caps with MDA alone and BSDA to give similar prepolymers to those discussed in Section 2.1.1 of this report. Each resin was prepared at a 40% w/w solids loading in dimethyl formamide by blending of the ingredients employing the methodology developed for the DONA system. The solid prepolymer products were isolated by removing DMF under vacuum and heat (200°F). Infrared analysis of the products at this point displayed carbonyl bands in the infrared regions of 1710 - 1720 cm^{-1} and 1770 - 1780 cm^{-1}, indicative of some imide formation. However, for the MONA capped resin, the 1770 - 1780 cm^{-1} band was of lower intensity than expected giving some indication that the dehydration of amide-acid to the imide was incomplete. This result was not entirely unexpected, because the drying and dehydration temperature was held to a minimum to prevent the occurrence of any reverse Diels-Alder reaction. To obtain a fully imidized prepolymer, a sample of the methyl oxynadic prepolymer was chemically dehydrated with acetic anhydride in DMF as confirmed by

IR (*i.e.*, an increase in intensity of the 1770 - 1780 cm^{-1} band). Both imidized prepolymer samples were found to be soluble in DMF at 40% w/w level.

The prepolymers obtained above were subjected to pyrolytic polymerization in a sealed tube employing conditions of 400°F, 200 psig and four-hour cure. Each prepolymer yielded a cured residue in the form of a consolidated plug which contained some voids caused by the evolution of volatile matter during cure. The samples were found to be insoluble on boiling at 20% w/w solids in DMF indicating crosslink formation. Each cured sample was subjected to thermogravimetric analysis (TGA). The ONA sample displayed good stability and a sharp break occurred in the TGA curve at 707°F. The MONA samples gave two different results. For the thermally dehydrated sample, two breaks were observed in the TGA curve. The first break occurred at 503°F followed by a ∿12% weight loss to a final major break at 773°F. The first weight loss is attributed to loss of water of imidization or trapped volatiles (*e.g.*, methylfuran). The MONA sample treated with acetic anhydride behaved like the ONA sample and displayed only one break at 750°F. These preliminary results (see Table IV) indicated that both resins would meet the thermo-oxidative

TABLE IV.

TGA SCREENING OF CURED POLYMER SAMPLES

Formulation	Formulated[a] Molecular Weight	Initial Thermo-oxidative[b] Stability of Cured Resin, °F
ONA/80MDA:20TDA/BSDA	1199	707
MONA/80MDA:20TDA/BSDA	1227	503 (1st) 773
MONA/80MDA:20TDA/BSDA[c]	1227	750

[a] Formulated on following molar basis; 2 end caps/2 diamines/BSDA.

[b] TGA conditions employed were scan rate of 5°F/min and 100 ml/min air flow.

[c] Chemically dehydrated with acetic anhydride.

requirements of the program. However, isothermal aging of the ONA and MONA derived polymers in air at 365°F and 450°F for up to 1000 hours (see Figure 1) showed these products to be significantly inferior to resins prepared employing DONA as an end-cap. Consequently, no further evaluation of alternative end-caps was performed. If ONA or MONA had produced polymers of equal or improved stabilities to DONA, then a viable alternative to a stable monomethyl ester for the PMR approach may have existed (see Section 2.1.4.2).

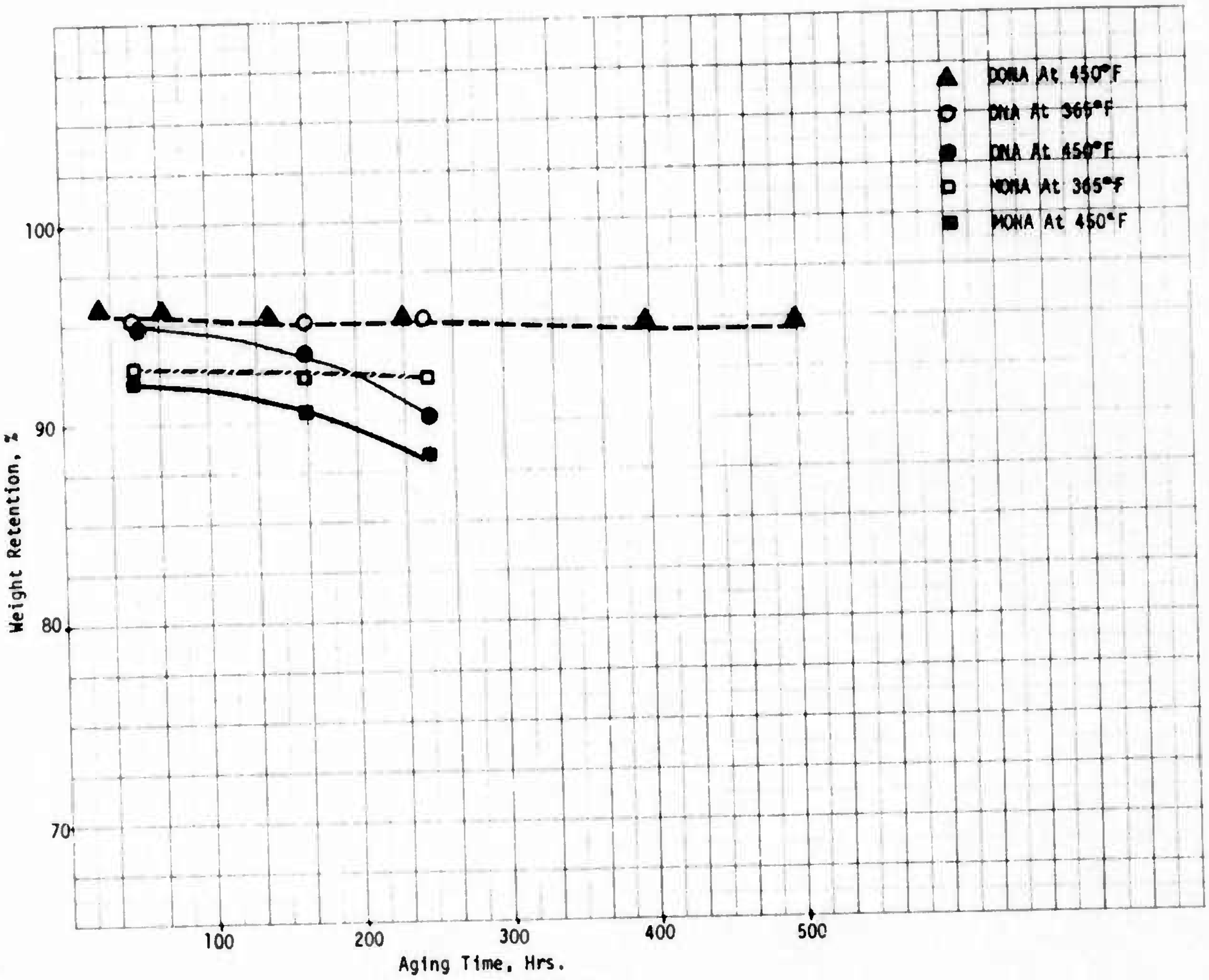


Figure 1. Weight Retention of ONA, MONA and DONA End Capped Polyimides During Isothermal Aging

2.2 TASK II - PROCESS DEVELOPMENT

Process development studies were performed in order to define suitable autoclave molding cycles for fabricating composites using the resins described in Section 2.1. Preliminary evaluations were performed of glass fabric prepregs using an Audrey II dielectrometer to determine optimum cure temperatures. Modifications were made to the procedures developed in Phase I (Reference 1) in order to obtain removal of volatile matter (solvent and reaction products), good consolidation, low void content and optimum cure of the polymer. Simultaneously, resin studies were continued during which several modifications were made to the resin system (see Section 2.1). Consequently, further process adjustments were necessary to accommodate each change in the resin system. Finally, mechanical properties of the resulting composites were determined and are reported in this section.

2.2.1 Audrey Dielectrometer Studies

In order to determine the temperatures at which polymeric relaxations or solvent removal occurs, studies were performed using the Audrey dielectrometer. During these studies, variation in the dissipation factor was measured as a function of variation of temperature. Changes of dissipation factor of the DONA prepregs during thermal cycling indicated phase changes (*i.e.*, polymer melt and flow) and/or chemical reaction (*i.e.*, chain extension and/or crosslinking).

Prepreg was prepared from Style 181 E-glass fabric, A1100 finish and the polyimide or PMR resin varnish to be evaluated. After drying, the prepreg was cut to 2-inch by 2-inch dimensions, stacked six-ply thick with a thermocouple located between the third and fourth plies, and then placed between two plies of pre-mold released, 0.003-inch thick Kapton film. Aluminum foil electrodes were located on the top and bottom of the stack with additional layers of Kapton film as insulators and then the assembly was inserted into a cold press (see Figure 2). Six plies of dry 181 glass fabric were placed on top of the assembly and the press was closed to the desired pressure (100 psi). The Audrey II dielectrometer and a Moseley Model 7030 x-y recorder were connected to the assembly in accordance with the wiring diagram in Figure 3 in order to plot changes.

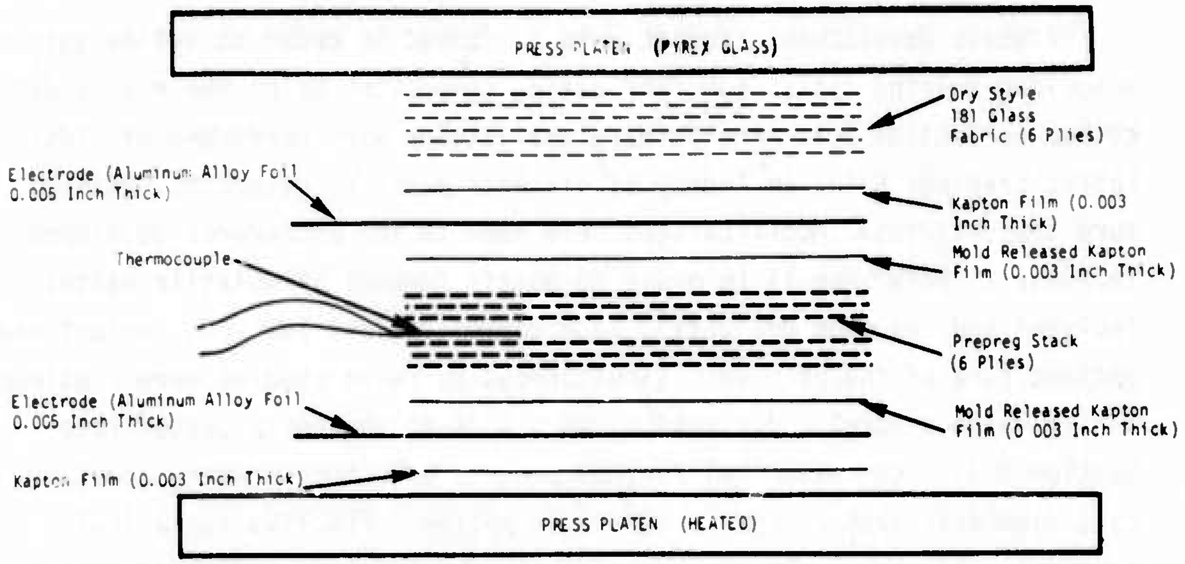


Figure 2. Schematic of Dielectrometer Screening Assembly

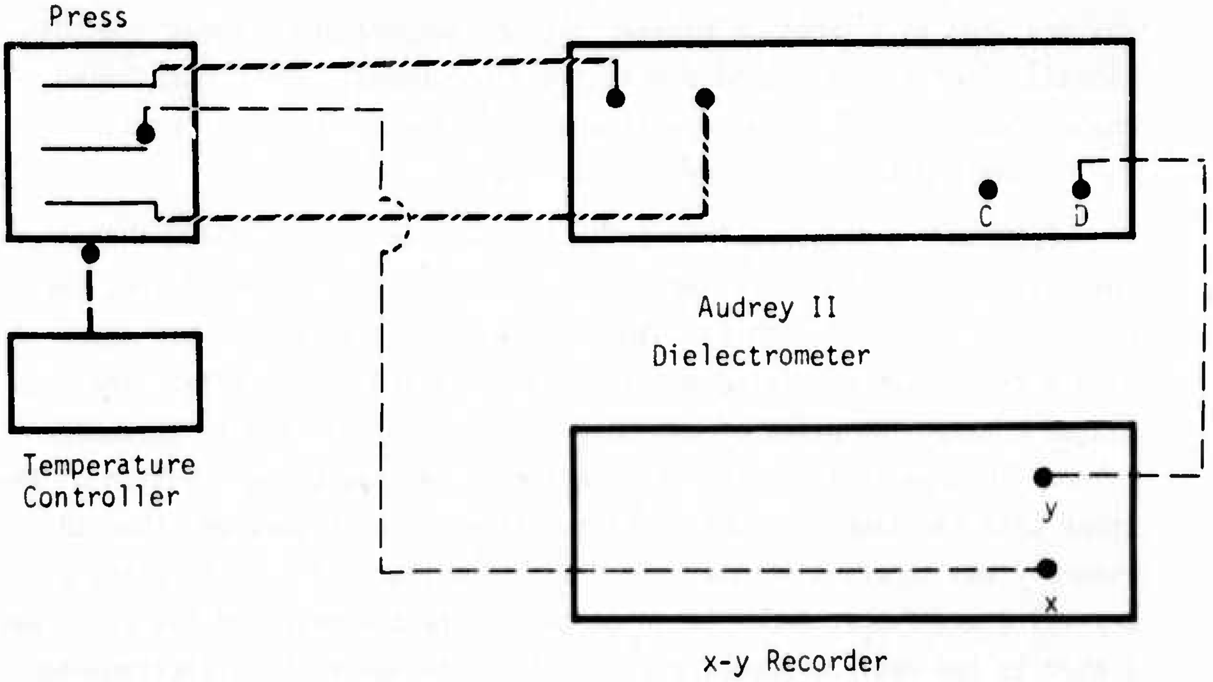


Figure 3. Wiring Diagram for Dielectrometer Experiments

The dielectrometer scan of DONA polyimide resin (imidized) in DMF (see Figure 4) shows that the main transitions occur at approximately 220°F and 450°F. A third peak which occurs in the upper 400°F range appears as a shoulder on the 450°F peak. The lower temperature peaks correspond to phase transitions and the highest temperature peak probably corresponds to post-curing of the DONA end-cap. On this scan it is difficult to assign solvent removal with any of the peaks. The Audrey scan of the PMR DONA/ dimethyl ester of BSDA/MDA in DMF (see Figure 5) shows no relaxation below 400°F associated with cure of the resin system, unless this is masked by the removal of solvent. The main peak occurs at 400°F and continues into a shoulder which again probably is associated with post-cure of the end cap. Scans of the PMR resin systems in methanol solvent are shown in Figures 6 and 7. In Figure 6 a scan of the original preparation of the dimethyl ester of BSDA is shown and Figure 7 shows a scan of the resin containing purified dimethyl ester of BSDA. Form of both of the scans is similar with a main low temperature peak at approximately 120°F which probably corresponds to formation of the amide acid. The secondary peak occurs at 295°F for the first resin system and at 260°F for the resin system containing the purified BSDA ester which probably corresponds to cure of the resin. These scans of the PMR resin system in methanol show the absence of high temperature peaks which could indicate that no post-cure reaction occurs. This was corroborated by the mass spectrometer analysis of the resin, which clearly shows that large amounts of 2,5 dimethyl furan are present at all temperatures above 110°F. Because 2,5 dimethyl furan is a by-product which forms from the reverse Diels-Alder reaction of the end-cap, it was assumed that the DONA end-cap was degrading in the presence of methanol prior to cure.

2.2.2 Processing Studies

Processing studies were performed to develop an autoclave molding process for graphite fiber prepregs containing a PMR-DONA resin. Promising mechanical properties (see Table V) were obtained from a composite panel molded as follows:

a) Room temperature to 250°F at 10°F minute without augmented pressure, plus 30 minutes at 250°F.

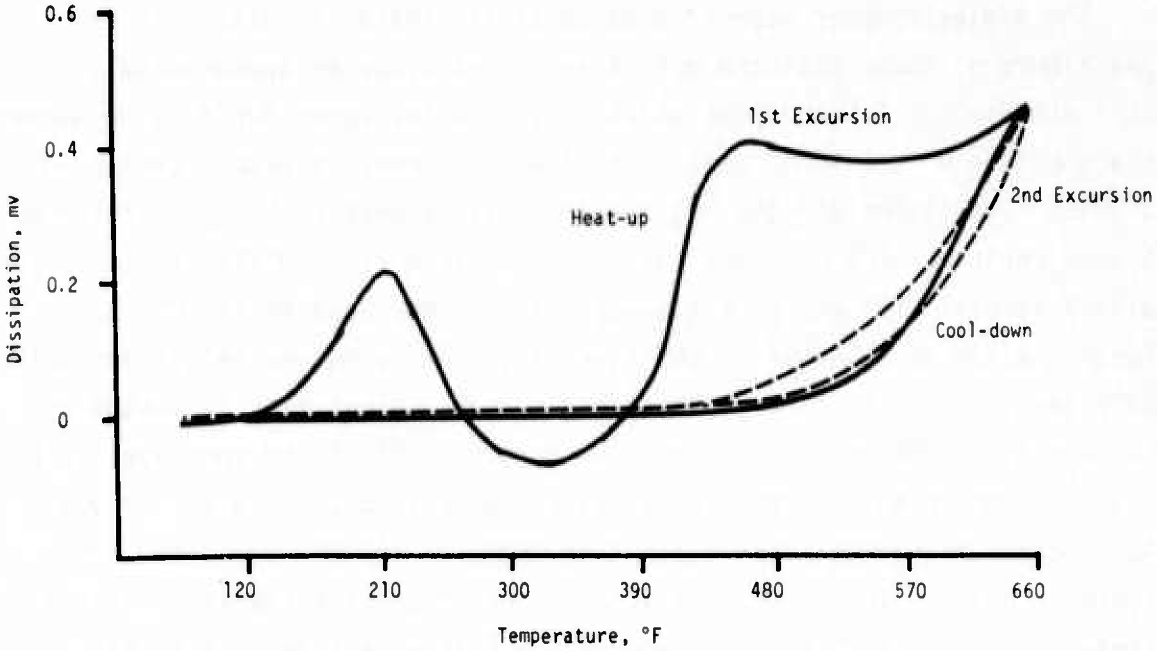


Figure 4. Audrey Dielectrometer Scan of DONA Imidized Resin

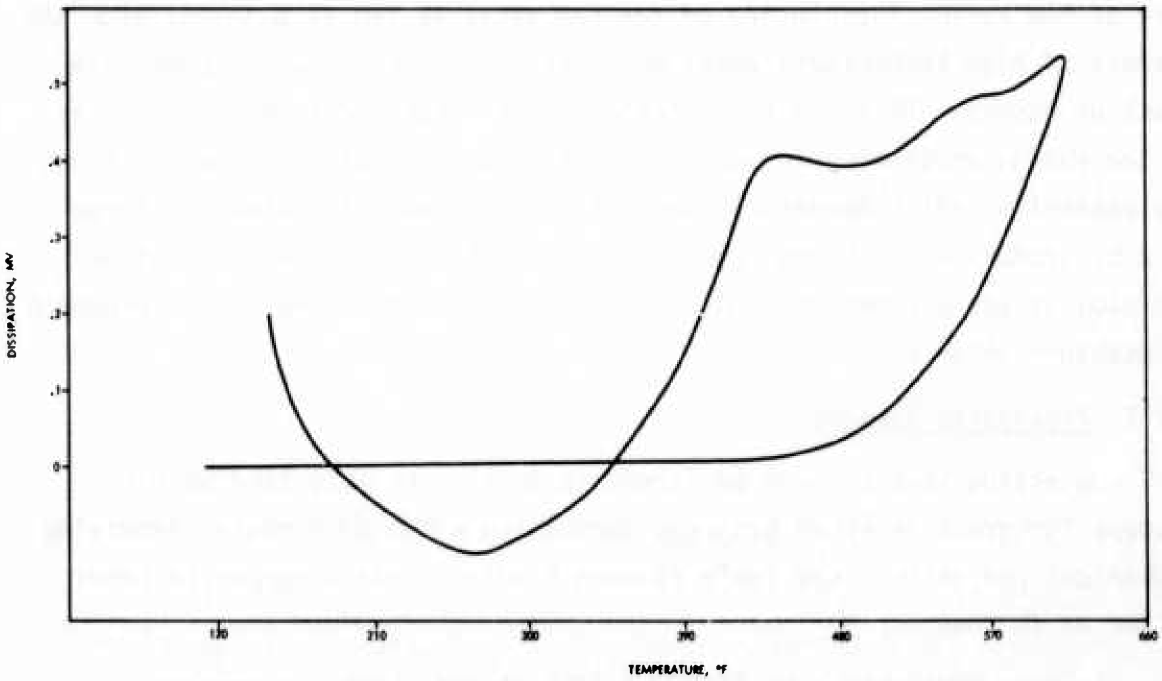


Figure 5. Audrey Dielectrometer Scans of PMR Resin in DMF.

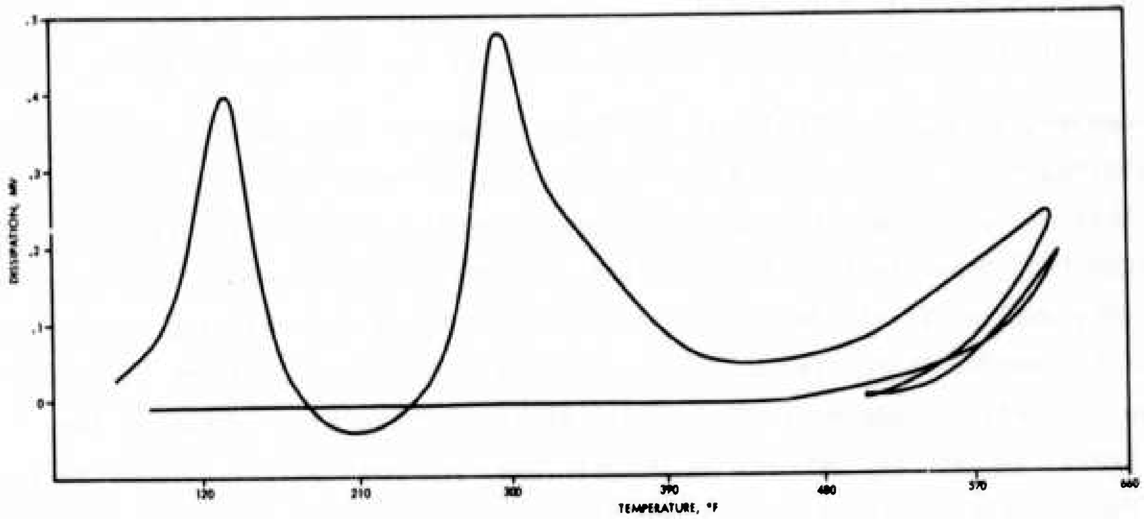


Figure 6. Audrey Dielectrometer Scan of PMR Resin in Methanol

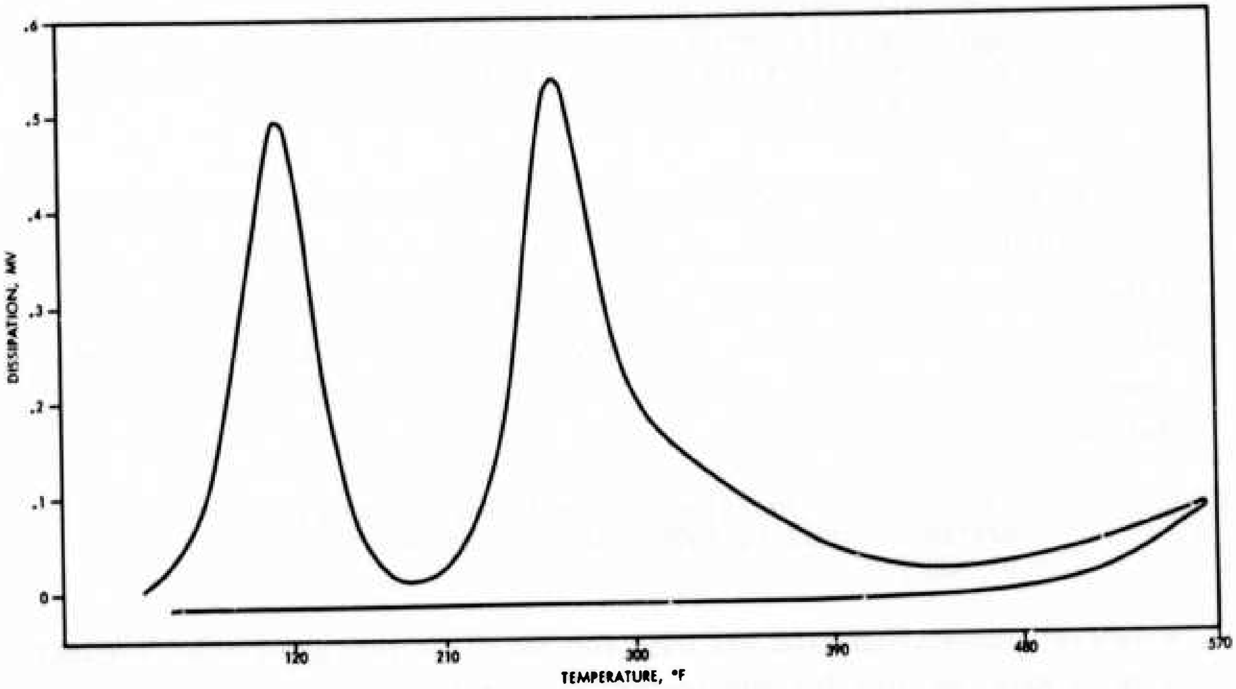


Figure 7. Audrey Dielectrometer Scan of PMR Resin Made Using Purified Dimethyl Ester of BSDA (In Methanol)

b) 100 psig positive pressure was applied then 250°F to 300°F at 10°F/minute.

c) After 30 minutes at 300°F, the temperature was raised to 400°F at 10°F/minute.

d) Post cure in an air circulating oven for 16 hours at 475°F.

However, as shown in Table V, the fiber volume of this panel was too high (target value is 55% v/v) signifying excessive resin flow. Based upon these and previous results, it appeared that this excessive resin flow was occurring prior to significant reaction between the monomeric reactants. Consequently, it was decided to examine approaches for reducing resin flow of the monomeric reactants. Two experiments then were performed in order to evaluate the use of a thixotropic agent in these experiments at two levels; two and one percent by weight based on resin solids. The results from these experiments (see Table VI) indicated that the thixotropic agent reduced resin flow but also resulted in a higher void content. Consequently, experiments were performed to evaluate lower levels of Cab-O-Sil (*i.e.*, 0.5 and 0.25% w/w) using the following cure cycle:

> Room temperature to 250°F at 10°F/minute without augmented pressure, then 30 minutes at 250°F. Apply 100 psig pressure and increase temperature to 300°F at 10°F/minute, then 30 minutes at 300°F. Raise temperature to 400°F at 10°F/minute and hold for one hour.

A second cure cycle also was evaluated which was similar except 5-8°F/minute heat-up rates were used. All four panels showed low resin flow and blistered during the 16 hour/475°F post cure cycle which was attributed to prepreg aging. Consequently, fresh prepreg was prepared from resin containing no Cab-O-Sil. Composites were made using the following molding cycle:

> Apply 100 psi positive pressure plus vacuum bag pressure. Heat to 250°F and hold for 60 minutes at 400°F.

A 10°F/minute heat-up rate was used for the first panel and a 3-5°F/minute heat-up rate was used for the second. Excessive flow was observed during cure, and after post cure the resulting panel's flexural properties were low due to excessive resin flow. Further processing studies were held in

TABLE V.

PRELIMINARY EVALUATION OF DONA PMR SYSTEM

PROPERTY	VALUE
FLEXURAL STRENGTH, KSI	
at R. T.	202
at 365°F	152
STRENGTH RETENTION, %	75
SHEAR STRENGTH, KSI	8
FIBER VOLUME, % V/V	67
VOID CONTENT, % V/V	1

TABLE VI.

THIXOTROPIC AGENT EVALUATION

Property	Value	
	Panel A[a)]	Panel B[a)]
Prepreg		
Resin Content, % w/w	42.2	38.7
Volatile Content, % w/w	8.9	8.8
Cured Composite		
Flexural Strength, Ksi		
at R. T.	187.5	185.6
at 365°F	128.0	153.8
Strength Retention, %	68.3	82.9
Shear Strength, Ksi	7.9	10.2
Fiber Volume, % v/v	63.4	62.5
Void Content, % v/v	6.3	5.8

[a)] Panel A resin matrix contains 2% w/w Cab-O-Sil
Panel B resin matrix contains 1% w/w Cab-O-Sil

abeyance at this point in time pending the results of the PMR/DONA resin studies described in Section 2.1.4.

The results from these resin studies indicated that it was not feasible to produce the mono-ester of DONA. Therefore, composite processing work was continued with a resin consisting of the DONA/MDA amide acid and the BSDA diester in a methanol solution. The only change in this resin to that used previously was the higher purity of the BSDA diester (see Section 2.1.4).

Prepreg tape was prepared with the new resin (without Cab-O-Sil) and a composite panel was autoclave molded by the first process described in this section. The resultant composite was unconsolidated indicating low resin flow. Consequently, additional processing studies then were performed (see Table VII).

These studies systematically evaluated the variables of prepreg tape volatile matter content, point in the cure cycle for application of pressure, and vacuum bag pressure cycle in order to control resin flow and to obtain good prepreg consolidation. Because the new PMR resin containing the purified dimethyl ester of BSDA reacted very rapidly, high prepreg volatile content and early application of pressure were necessary in order to consolidate the panels. The mechanical properties of the most promising panel obtained from this system were low *i.e.*, flexural strength ~100 Ksi and shear strength ~5 Ksi.

Another attempt was made using the same PMR resin system in order to determine whether acetone would provide improved DONA end-cap stability and thus result in void-free panels. The same cycle as Run #VIII in Table VII was used to mold a composite panel. Mechanical properties of the panel fabricated by this method were determined and again were low, *i.e.*, flexural strength ~80 Ksi and shear strength ~5 Ksi.

The high void content (~10%) obtained in panels produced from PMR resins in both acetone and methanol probably can be attributed to the continued liberation of 2,5 dimethyl furan as the DONA end-cap degrades (see Section 2.2.1). Consequently, further work with the PMR type of DONA resin is not warranted on this program. Therefore, continuing Task II studies will evaluate variations in molecular weight and other formulary

TABLE VII.

CURE CYCLE SCREENING FOR OPTIMIZED DONA PMR RESIN

Run #	Prepreg Tape Volatiles	Cure Cycle[1]	Postcure	Results
I.	6%	FV, 190°F (30m) → 250°F(15m) → 100 psi P → Δ to 300° → 300°(60m) → 400°(60m)	A	Unconsolidated
II.	6%	FV, 190°F (30m) → 250°, FV, 100 psi P → 250°(30m) → 300°(60m) → 400°(60m)	A	Unconsolidated
III.	6%	FV, 190°F (30m) →,100 psi P → Δ to 250° → 250°(30m) → 300°(60m) → 400°(60m)	A	Unconsolidated
IV.	6%	FV, 100 psi P, 190°F(30m) → , 250°(30m) → 300°(60m) → 400°(60m)	B	Unconsolidated
V.	15%	FV, 100 psi P, 190° (30m) → , 250°(30m) → 300°(60m) → 400°(60m)	C	Excess resin flow
VI.	10%	HV, 60 psi P, 190°F(30m) → FV, 250°(30m) → 300°(60m) → 400°(50m)	C	Excess resin flow
VII.	13%	HV, 190°(30m) → 250°, 60 psi P → 250°(30m) → 300°(60m) → 400°(60m)	C	High void panel
VIII.	13%	HV, 190°(30m), 20 psi P → FV, 250°, 70 psi P → 250°(30m) → 300°(60m) → 400°(60m)	C	Most promising panel

[1] Postcure cycles -
A - 16 Hours, 475°F
B - 16 Hours, 400°F at 100 psi, then 16 Hours 350°F, 4 Hours 425°F
C - 16 Hours, 350°F, 4 Hours at 400°F, 3 Hours at 450°F

HV = Half Vacuum Pressure (~7 psia)
FV = Full Vacuum Pressure (~14 psia)
P = Pressure

variations of DONA polyimide prepolymer solutions in DMF in order to improve the toughness of DONA composites. It is anticipated that improved toughness also will result in higher shear strengths than obtained earlier during Phase I studies (Reference 1).

2.3 TASK III - PRELIMINARY INGREDIENT AND RESIN SCALE-UP PRODUCTION

During Phase I all ingredients, *i.e.*, DONA and BSDA and their derivatives (see Section 2.1.1 and Appendix I) were prepared in laboratory bench-top quantities of 1/4 pound to 1-1/2 pounds. This scale obviously would not be cost-effective during continuing program efforts requiring fabrication of large panels. Also, it is very difficult to assess reproducibility of a new resin if small (∿1 pound) batches of polymer are used.

Consequently, a scale-up facility was designed, assembled and checked-out in readiness for large batch resin production. This multipurpose TRW facility for monomer/polymer scale-up is shown in Figure 8. The flask shown is a 72 liter self-contained unit which will be capable of producing material in suitable quantities for reproducibility and/or commercial feasibility studies of ingredient or resin preparation methods. The facility will accommodate up to four of the flasks shown in Figure 8.

Figure 8. BSDA Scale-up Facility

During the continuing program reported herein, batches of BSDA or its dimethyl ester in ∿10 pound quantity will be produced employing the TRW synthesis process. Similarly, it will be possible to prepare up to 12 gallons of resin varnish assuming a 30% w/w solids loading is defined to be an optimum concentration.

III. PHASE III - ADHESIVE EVALUATION

Two different non-condensation curing mechanisms for polyimide resins were identified during Phase I:

- DAS Resin - Polyimide prepolymers which contain 4,4'-diaminostilbene (DAS) in their backbone which, through its unsaturation provides crosslink cure sites.
- DONA Resin - A-type polyimide end-cap technology except that an oxynadic anhydride is used instead of the previously used nadic anhydride.

Both of these approaches for adhesive resins were evaluated during Phase III as described below.

3.1 DAS RESIN EVALUATION

The most promising DAS resin identified during Phase I studies consisted of BSDA/60MDA:10DAS:30PED (400 MW). Therefore, this formulation was selected for evaluation during Phase III. A small quantity of this resin was prepared in accordance with the procedure described in Appendix I. During preparation, extreme difficulty was experienced in making a resin solution using the 400 MW PED and severe precipitation of the resin occurred within several hours of preparation. However, in order to obtain an evaluation of the DAS resin for adhesive applications, aluminum alloy lap-shear panels (see Figure 9) were prepared for bonding using standard alkaline clean and sulfuric acid/sodium dichromate etch procedures. These procedures consisted of an alkaline clean (15 minutes at 180°F in Turco HTC) followed by immersion for 15 minutes at 150°F in a bath consisting of:

Sodium Dichromate (Federal O-S-595A)	28.5 g
Sulfuric Acid (Federal O-A-115 Class A, Grade 2)	285 g
Water	to make one liter

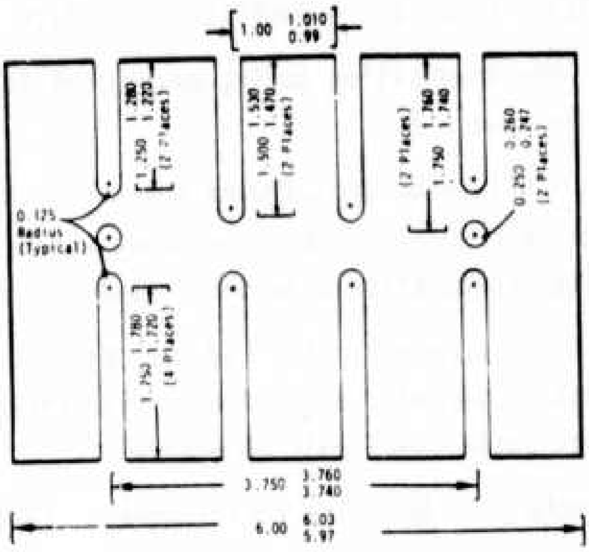


Figure 9. Lap-Shear Panel

After rinsing in distilled water, the faying surfaces of the lap-shear panels were dried and then coated with a thin film of the DAS resin. This coating was dried for 60 minutes at 180°F in an air circulating oven. An adhesive film was prepared by coating Style 112 glass fabric, A1100 amino silane finish with the DAS resin (no filler). This also was dried for 60 minutes at 180°F in an air circulating oven. During the preparation of the adhesive film, severe precipitation occurred in the DAS resin solution.

The lap-shear panels were bonded together by placing one layer of the adhesive film between the faying surfaces. The joints were mated and assembled in a bonding jig. These assemblies were press-bonded at 400°F for one hour under 100 psig pressure and then postcured in an air circulating oven for 16 hours at 475°F. Lap-shear strengths of the resultant panels were determined but the values obtained were very low (∿290 to 580 psi). However, this was attributed to poor resin quality as displayed by severe precipitation in the resin solution. Additional specimens then were prepared and evaluated using a DAS polyimide resin containing commercially available 600 MW PED (Jeffamine). Again, useful lap-shear strength values were not obtained (*i.e.*, <500 psi) demonstrating no resin improvement by substitution of the higher molecular weight, commercially available PED. Consequently, it was decided to concentrate the adhesive evaluation activities on DONA type resins.

3.2 DONA RESIN EVALUATION

DONA resin consisting of the dimethyl ester of BSDA, DONA and MDA in methanol (50% w/w) was prepared as described in Section 3.1. Because the viscosity of the resin/solvent was low, Style 120 E-glass fabric was used between the faying surfaces of the aluminum panel to control the resin flow during cure. The aluminum panels were prepared as described in Section 3.1 and immediately primed with DONA resin. Glass fabric was placed on one resin surface and also coated with DONA resin. These panels then were assembled and placed in an adhesive bonding jig for curing. One set of panels was cured for 30 minutes at 190°F, followed by 30 minutes at 250°F, 30 minutes at 300°F, 60 minutes at 400°F and postcured for 16 hours at 400°F. The second set of panels was cured for 30 minutes at 250°F, followed by 30 minutes at 300°F, 60 minutes at 400°F and postcured for 16 hours at 400°F. Lap-shear strength values for the two sets of panels were 1750 and 1650 psi, respectively. These values indicate high promise for the DONA resin system as an adhesive. Therefore, development work will continue on DONA resin optimization and adhesive formulation during the next 12-month period.

IV. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during the first twelve-month effort in Phase II and III of the exploratory development of processable laminating resins with improved toughness and moderate temperature capability. Based on these findings, recommendations are given for continuing resin, composites and adhesives development studies.

4.1 CONCLUSIONS

1. Resin systems containing DONA, BSDA and MDA provided equivalent processability and end-properties to the previously developed resins containing TDA in addition to the above constituents. Consequently, it was concluded that TDA is not required in DONA resin formulations containing BSDA.
2. Alternative oxynadic end-caps to DONA, such as ONA and MONA, did not provide thermally stable resins equivalent to the cured DONA end-capped resin system. Consequently, it was concluded that DONA is the most promising low temperature curing end-cap for A-type polyimide resins identified at this point in time.
3. Attempts to identify lower boiling solvents than DMF or NMP were unsuccessful. The unsuccessful studies included evaluation of NMP co-solvents, attempts to identify NMP low boiling azeotropes and evaluation of DONA resin using the PMR approach with methanol and acetone. It was established previously that NMP cannot be removed completely from the resin matrix in composites and that the residual NMP plasticizes the resin. Consequently, it was concluded that DMF is the most promising solvent for DONA polyimide resins identified at this point in time.
4. Evaluation of DAS and DONA resin systems for structural bonding of metal adherends indicated low probability of success with the DAS resins and high promise for

the DONA resin. Consequently, it was concluded that the DONA end-capped polyimide resin systems are the most promising candidates for detailed adhesives studies.

4.2 RECOMMENDATIONS

1. Further resin studies with DONA polyimide prepolymers in DMF solutions are warranted. These studies should be concerned with improving the toughness of the resin system in order to provide higher shear strength and fracture toughness values for graphite fiber reinforced composites than those obtained earlier. 5
2. Development of molding processes for large panel fabrication and determination of mechanical properties for large composite panels are warranted. These studies should be performed with the most promising resins identified during the studies described above.
3. Development of adhesive resin formulations and compounds based on the DONA resin identified in (1) above are warranted. Studies should include resin optimization,adhesive formulary, process development and detailed evaluation. Evaluation tests should include lap-shear, T-peel and stress-rupture measurements at -65°F, R.T., and 365°F.

V. REFERENCES

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APPENDIX I.
PREPARATION OF MONOMERS & POLYMERS

I.1 REACTION OF 1,4-DIMETHYL-7-OXYNADIC ANHYDRIDE (DONA) WITH SODIUM METHOXIDE

A 100 ml, 3-necked flask equipped with mechanical stirrer, condenser, addition funnel and nitrogen inlet was flushed with nitrogen and charged with 3.68 g (0.02 mole) DONA in 35 ml of methanol and cooled in ice-water. To it was added 1.08 g (0.02 mole) of sodium methoxide in 35 ml of methanol within 10 minutes. The clear solution was stirred at 32°F for 8 hours. Methanol then was evaporated from an ice-water bath by rotary evaporation to yield 5.7 g of white, very hygroscopic solid. This solid was redissolved in methanol and 1.46 g (0.04 mole) of dry hydrogen chloride was bubbled into the stirred solution at 32°F during five minutes. A small amount of NaCl precipitated. The mixture was filtered and the filtrate was evaporated from ice-water bath. The residue was 2.0 g of green liquid which became very dark after several hours. The NMR spectrum of this liquid indicated that considerable reverse Diels-Alder reaction had occurred.

I.2 REACTION OF BSDA WITH METHANOL

A 300 ml, 3-necked flask with mechanical stirrer, condenser and nitrogen inlet was charged with 10.84 g (0.02 mole) of BSDA and 100 g (3.1 moles) of methanol. The white suspension was brought to reflux and gradually became clear during five hours. After 5.5 hours the clear solution was evaporated to dryness by rotary evaporation yielding 12.0 g of foamy white solid, mp 230-238°F. Analysis of the NMR spectrum of this solid indicated fewer methyl groups per molecule than required for the desired dimethyl ester.

A similar reaction run for 45 hours at reflux yielded a white solid with the same deficiency of methyl groups.

I.3 REACTION OF BSDA WITH SODIUM METHOXIDE IN BENZENE

A 300 ml, 3-necked flask equipped with mechanical stirrer, condenser and nitrogen inlet was charged with 10.84 g (0.02 mole) of BSDA and 75 ml of benzene. To the white suspension was added in small portions at room temperature 2.16 g (0.04 mole) sodium methoxide suspended in 60 ml of benzene (no change in temperature was noted). The mixture was stirred at room temperature for one hour then at reflux for 2.5 hours. It then was cooled to room temperature and 40 ml of 1.0 N aqueous HCl (0.04 mole) was added with stirring. Filtration yielded a sticky, white precipitate. To remove sodium chloride, this solid was suspended in distilled water and filtration was attempted. Filtration was unsuccessful using either vacuum or pressure due to the sticky nature of the solid. Consequently, it was dried thoroughly in a vacuum oven yielding a solid which melted at 455-463°F.

I.4 REACTION OF BSDA WITH SODIUM METHOXIDE IN METHANOL

A 300 ml, 3-necked flask equipped with mechanical stirrer, addition funnel, condenser, and nitrogen inlet was charged with 5.42 g (0.01 mole) of BSDA and 50 ml of methanol. Sodium methoxide (1.08 g, 0.02 mole) in 50 ml of methanol was added to the stirred suspension during ten minutes. It then was heated to reflux. The mixture became clear in one hour; refluxing was continued for four hours. It then was cooled to room temperature and 1.46 g (0.02 mole) of dry hydrogen chloride was bubbled in. After stirring 15 minutes the solvent was evaporated on a rotary evaporator then in a vacuum oven at 194°F to yield 6.2 g of white solid, mp 230-265°F with decomposition.

I.5 PREPARATION OF DONA PMR LAMINATING VARNISH

To a stirred solution of 19.8 g (0.10 mole) of MDA in 100 g of methanol was added 19.8 g (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 30.3 g (0.05 mole) of BSDA dimethyl ester. The last traces of the ester were washed into the flask with an additional 65 g of methanol. The varnish was maintained under a nitrogen blanket and used to prepare prepregs within three hours of preparation.

I.6 PREPARATION OF BSDA/60MDA:10DAS:30PED (MW 400) RESIN

A mixture consisting of 3.57 g (0.018 mole) of MDA, 0.63 g (0.003 mole) of DAS and 3.60 g (0.009 mole) of 400 MW PED was dissolved in 60 ml of DMF and placed in a microblender. To the stirred solution was added slowly 16.26 g (0.030 mole) of powdered BSDA. The mixture was stirred for an additional ten minutes after complete addition of the dianhydride to give a clear solution. The imidized polymer was isolated by drying under vacuum at 264°F (129°C) for 16 hours.

I.7 PREPARATION OF BSDA/60MDA:10DAS:30PED ADHESIVE VARNISH

A 2.0 g sample of the DAS containing polyimide was dissolved in 12 g of DMF. The solution then was filtered through glass wool to remove a few small pieces of insoluble material. Solvent was allowed to evaporate to give a 17% (w/w) solids varnish. To the varnish were added 0.0465 g (0.00013 mole) of *bis*(4-maleimidophenyl) methane (BMPM) and 0.151 g (0.00052 mole) of Lupersol 101. This varnish was used in the preliminary adhesive studies.

I.8 SYNTHESIS OF METHYL OXYNADIC ANHYDRIDE

To a stirred suspension of 49 g (0.5 mole) of maleic anhydride in 60 ml of anhydrous ether was added 45.1 g (0.55 mole) of freshly distilled 2-methylfuran. Stirring was stopped after four hours and the reaction mixture was allowed to stand for 48 hours. The precipitated Diels-Alder adduct, 1-methyloxynadic anhydride, was collected by filtration and dried *in vacuo* to give 88 g (98%) of anhydride; mp. 149-154°F (65-68°C).

The infrared spectrum (Figure 10) is consistent for the assigned structure. The carbonyl bands for the anhydride are present at 1780 cm^{-1} and 1840 cm^{-1}.

The NMR spectrum for the compound is shown in Figure 11. The assignment of the bands in the spectrum is as follows: vinyl protons appear as a multiplet centered at $\tau = 3.57$; the allylic proton is also a multiplet at $\tau = 4.73$; further upfield at $\tau = 6.80$ is the multiplet for the C-2 and

C-3 protons and the singlet at τ = 8.25 is assigned to the methyl group. The small peak at τ = 7.73 is attributed to either an impurity or more likely to the methyl group in another conformation due to the possibility of endo-exo confirmations of the adduct.

I.9 SYNTHESIS OF IMIDE PREPOLYMER FORMULATION MONA/80MDA:20TDA/BSDA (1227 FMW)

To a stirred solution of 6.35 g (32 mole) of methylene dianiline and 1.73 g (8 mole) of thiodianiline in 25 ml of DMF was added 7.21 g (40 mole) of methyloxynadic anhydride under a nitrogen atmosphere with cooling so as to maintain the temperature below 80°F. After the addition was complete, the mixture was stirred for an additional 15 minutes. To this solution was added a solution of 10.85 g (20 mole) of BSDA in 36 ml of DMF. The rate of addition of the anhydride was such that the temperature of the reaction mixture remained below 85°F. The mixture then was stirred for 30 minutes after the BSDA addition. The resulting amide-acid solution was taken to dryness *in vacuo* at 190°F and maintained at that temperature for a total of 16 hours. The infrared spectrum of this imide prepolymer is shown in Figure 12.

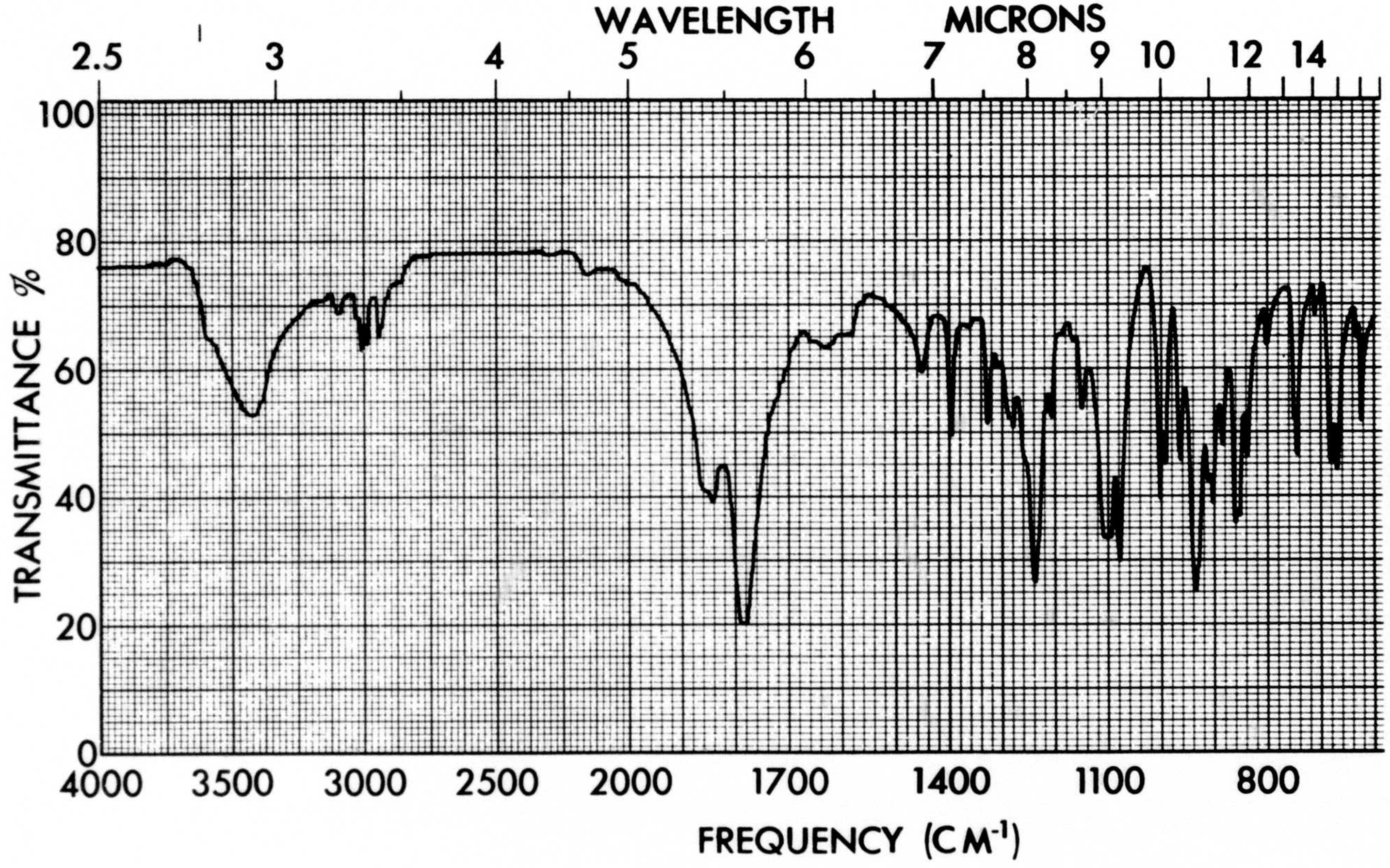

Figure 10. Infrared Spectrum of 1-Methyl Oxynadic Anhydride (KBr)
Concentration: 3.3 mg/g KBr

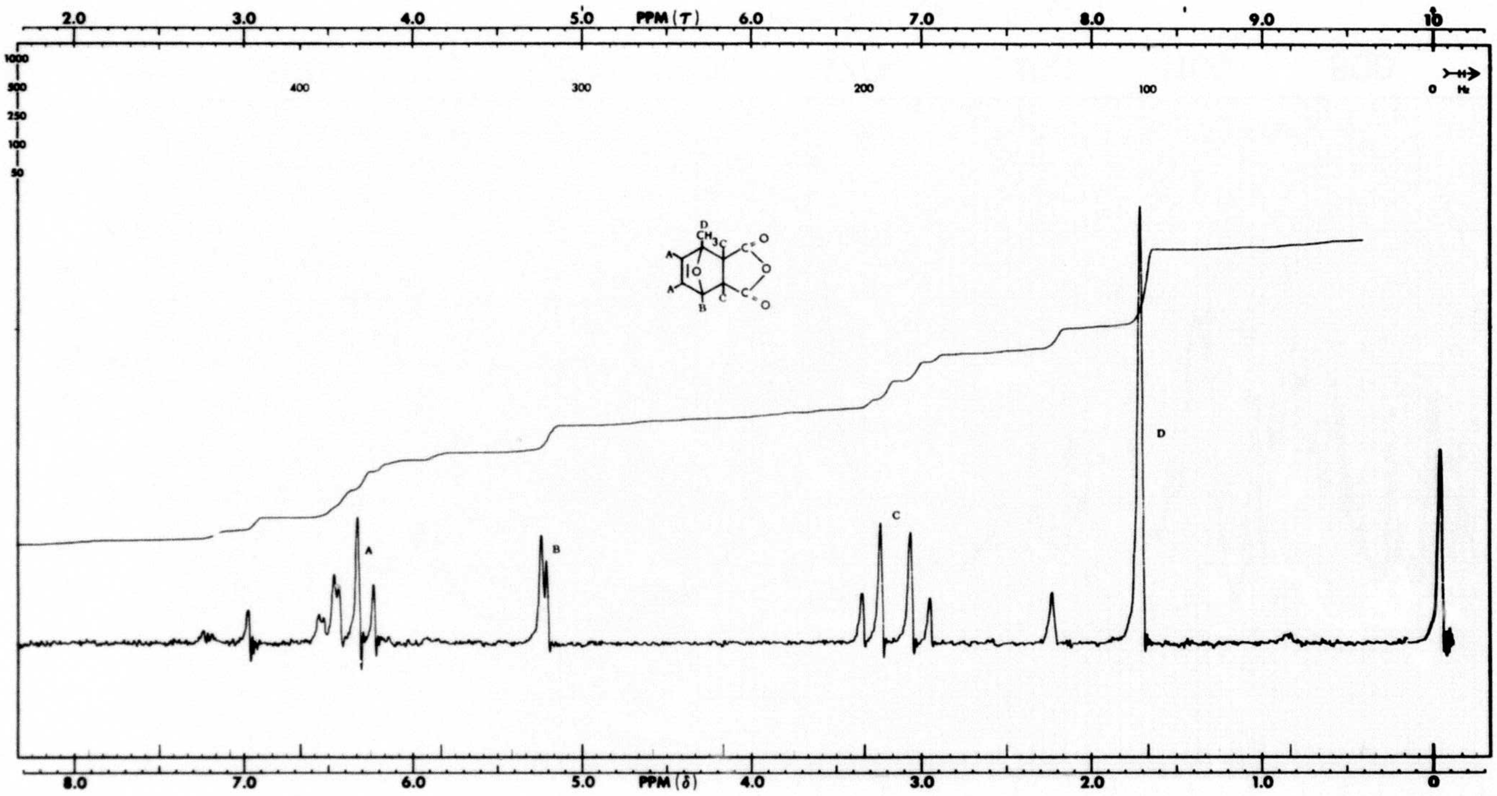

Figure 11. Nuclear Magnetic Resonance Spectrum of 1-Methyl Oxynadic Anhydride
Solvent: $CDCl_3$

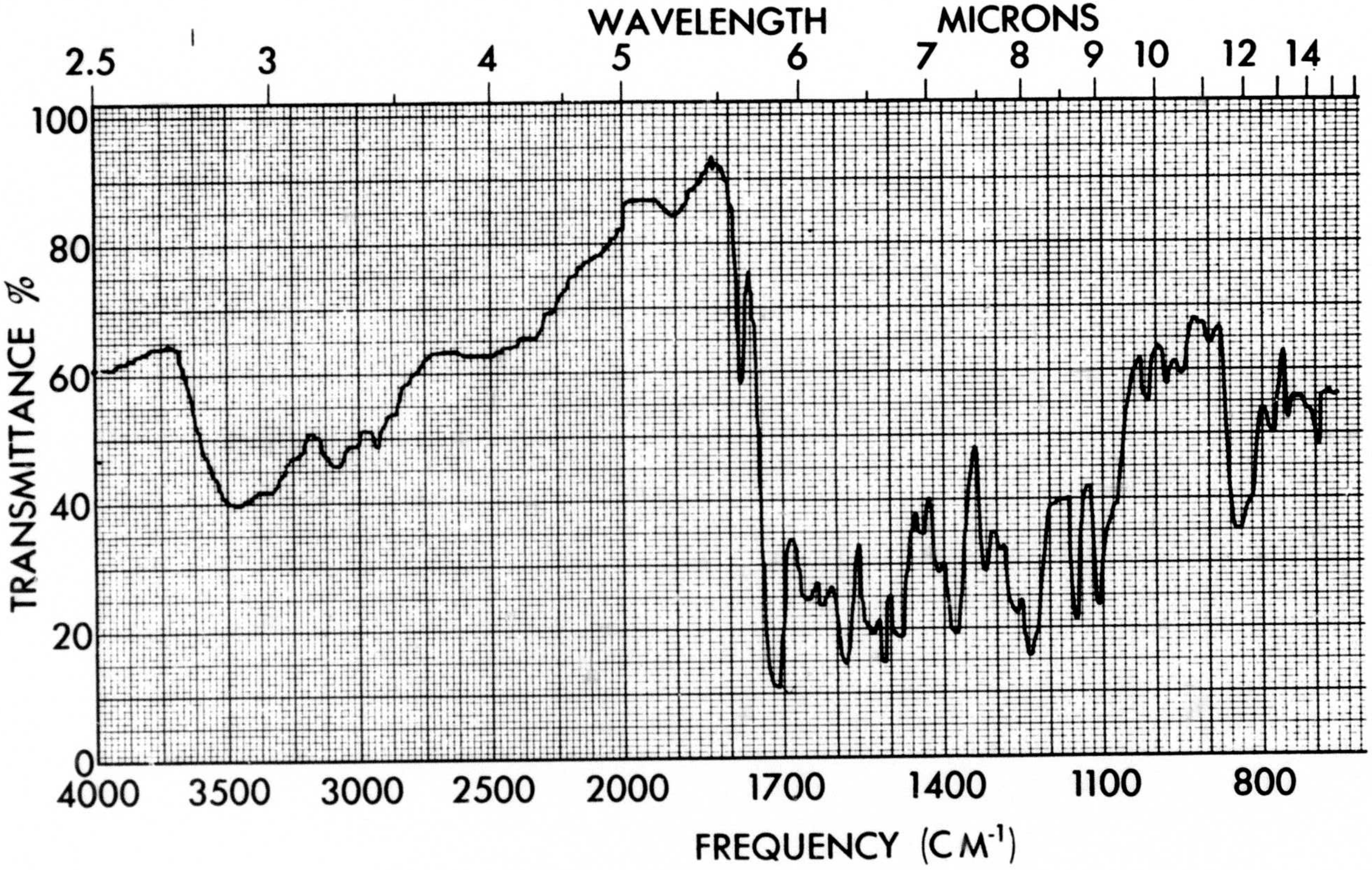

Figure 12. Infrared Spectrum of Imidized Prepolymer
Formulation MONA/80MDA:20TDA/BSDA (1227 FMW)
Concentration: 3.1 mg/g KBr

APPENDIX II.

PREPREG PREPARATION AND MOLDING PROCEDURES

II.1 PREPARATION OF DONA/A-S PREPREG

1. Install a layer of Mylar film on the drum of the winding machine.
2. Prepare a 30% w/w NMP resin solution of 1200 FMW DONA/80MDA:20TDA/BSDA and pour into the impregnation tank of the winding machine.
3. Wind Hercules A-S graphite fiber tows at 8 tows per linear inch on top of the Mylar film. Adjust resin metering bars to provide the desired resin pick-up.
4. Dry prepreg under infrared lamps placed 10 inch from surface of prepreg with drum rotating at 45 rpm for 72 hours.
5. Remove prepreg on Mylar film from the drum and cut into pieces 5 inch by 12 inch.
6. Dry prepreg without Mylar film in an air circulating oven for 150 minutes at 250°F.

II.2 PREPARATION OF DONA/GLASS FABRIC PREPREG

1. Immerse glass fabric with I545 or equivalent acrylosilane finish in a 30% w/w resin solution of 1200 FMW DONA/80MDA:20TDA/BSDA polyimide resin and NMP.
2. Draw impregnated fabric between stainless steel wiper bars with the gap set to provide the desired resin pick-up.
3. Dry prepreg in air for 2 hours at 250°F.

II.3 INSTALLATION OF VACUUM BAG

1. Lay-up prepreg to the desired thickness and then place 1-ply of perforated Teflon coated glass fabric on the top and bottom of the prepreg stack.

2. Lay 1-ply of dry Style 181 glass fabric over an aluminum alloy base plate and then place the prepreg on top.
3. Lay 4-ply Style 181 dry glass fabric on top of the prepreg stack.
4. Lay a flat aluminum alloy caul sheet on top of this assembly for flat laminates and lay 1-ply of Style 181 dry glass fabric on top of the caul sheet.
5. Place a bead of vacuum bag sealant such as Schnee Morehead High Temperature Sealant around the periphery of the base plate and then cover the assembly with green Vac-Pac or equivalent nylon film.
6. Seal the nylon film to the vacuum bag sealant and evacuate the air from inside the bag.

II.4 AUTOCLAVE MOLDING PROCEDURE

1. Install the vacuum bag assembly in an autoclave and evacuate the air from inside the bag.
2. Apply positive pressure of 100 psig nitrogen gas and raise the autoclave temperature to 400°F at a heat-up rate of 10°F/minute and hold for 2 hours.
3. Cool to room temperature under pressure.
4. Remove the cured panel from the autoclave and vacuum bag then postcure in an air circulating oven for 16 hours at 475°F.

APPENDIX III.

TEST PROCEDURES FOR CHARACTERIZATION OF PREPREG AND COMPOSITES

III.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

III.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

III.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.

III.4 DENSITY OF COMPOSITES

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

III.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.

III.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

III.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

III.8 SHEAR STRENGTH OF COMPOSITES (Reference 13 - Method 7.3.6.1)

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

III.9 FLEXURAL PROPERTIES OF COMPOSITES (Reference 13 - Method 7.3.8.1)

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

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

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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