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DEVELOPMENT OF AUTOCLAVABLE ADDITION-TYPE POLYIMIDES

by

R. J. Jones, R. W. Vaughan, M. K. O'Rell and
C. H. Sheppard

TRW
SYSTEMS GROUP

ONE SPACE PARK • REDONDO BEACH • CALIFORN

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NASA Lewis Research Center
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Tito T. Serafini, Project Manager

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16. Abstract

Two highly promising approaches to yield autoclavable addition-type polyimides were identified and evaluated in the program. Conditions were established for autoclave preparation of Hercules HMS graphite fiber reinforced composites in the temperature range of 473°K (390°F) to 505°K (450°F) under an applied pressure of 0.7 MN/m^2 (100 psi) for time durations up to four hours. Upon oven postcure in air at 589°K (600°F), composite samples demonstrated high mechanical property retention at 561°K (550°F) after isothermal aging in air for 1000 hours. Promise was shown for shorter term mechanical property retention at 589°K upon exposure in air at this temperature.

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FOREWORD

This document constitutes the final report for the work accomplished between 1 May 1972 and 1 September 1973 by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-15834 on Development of Autoclavable Addition-type Polyimides.

This work was conducted under the technical direction of Dr. Tito T. Serafini of the Lewis Research Center, Cleveland, Ohio.

The Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division was responsible for the work performed on this program. Dr. E. A. Burns, Manager, Applied Chemistry Department, provided overall program supervision and Dr. R. J. Jones was Program Manager. The Principal Investigator responsibilities for the program were performed by Mr. R. W. Vaughan. Major technical contributions throughout the program were provided by Mr. M. K. O'Rell and Mr. C. H. Sheppard. Acknowledgment is made of the technical assistance provided during the program by the following TRW Systems personnel.

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SUMMARY

This report is the final program report document describing work performed by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-15834. The objective of this program was to develop addition-type polyimide resins which would process or cure at a maximum of 505°K (450°F) and 1.4 MN/m^2 (200 psi) to give mechanically integral parts which could be removed from the autoclave and, if required, be final staged by postcure technology. The autoclave process condition objectives were accomplished by sequential program tasks which included 1) pertinent model compound polymerization studies, 2) polymer synthesis and characterization, 3) autoclave process screening, 4) resin/process development studies and 5) detailed long-term testing on the two novel resin approaches selected for study.

The first phase of the work involved synthesis characterization of new model end cap compounds possessing novel norbornene-type structures similar to nadic anhydride which was previously shown in Contracts NAS3-12412 and NAS3-13489 to undergo reverse Diels-Alder/pyrolytic polymerization. Initial model work showed that the new compounds possessing various substituents on the norbornene ring would undergo a reverse Diels-Alder reaction at temperatures less than or equal to the 505°K autoclave cure objective of the program. Although the desired reverse Diels-Alder step required for pyrolytic polymerization was achieved, the elements produced during the pyrolyses would not recombine to form a polymeric material possessing the desired 589°K (600°F) initial thermo-oxidative stability. Consequently, it was necessary to utilize other technology shown to be promising in previous studies at NASA/LeRC and TRW.

The last phase of the Task I model studies was devoted to proving the utility of new approaches to meet program objectives. It was shown that a bis(nadimide) could be precured at temperatures of approximately 505°K,

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which when treated by postcure at 589°K, gave a resin material meeting the objective 589°K initial thermo-oxidative stability. It was also demonstrated that a novel poly(Diels-Alder) (PDA) reaction of a bis(furanimide) compound and a bis(maleimide) can be effected at temperatures of approximately 477°K (400°F). This resin, on postcure at 589°K, also possessed the objective 589°K thermo-oxidative stability.

Polymer studies were then conducted which employed the new approaches. In order to utilize the demonstrated nadic precure reaction at 505°K, it was necessary to select a polymeric backbone structure that would show melt/flow/consolidation characteristics at 505°K suitable for fabrication of composites. An ideal approach to meet these requirements was the polymerization of monomeric reactants (PMR) developed at NASA/LeRC. The combination of ingredients selected for study were monomethyl nadic ester (NE)/methylene dianiline (MDA)/dimethyl ester of benzophenone tetracarboxylic acid (BTDE) at a stoichiometry level which would yield a 1500 g/mol formulated molecular weight (FMW) polymer. For the alternative PDA approach, the ingredients selected for study were bis(furfuryl) benzophenone tetracarboxylic imide (BFBI) and bis(4-maleimidophenyl) methane (BMPM).

Polymer studies were conducted employing the PMR and PDA resin approaches. It was shown that both systems could be processed at ≤505°K (450°F) to give well consolidated neat resin specimens, which when postcured at 589°K (600°F), possessed initial thermo-oxidative stabilities >589°K. Other reaction conditions were demonstrated (i.e., pressures and time durations) that showed promise for practical autoclave processability.

The results of the polymer study were employed to structure autoclave fabrication process matrices. AUDREY dielectrometer screening studies were conducted and process variable levels within program goals were conducted in an autoclave employing Hercules HMS fiber as a reinforcement. Autoclave methods suitable to prepare low void content laminates possessing high initial mechanical strengths at room temperature and 589°K were identified.

Studies were then conducted to investigate potential improvements in the resin structures and/or autoclave processes developed for each of the two polymer approaches. It was experimentally determined that new quinoxaline-imide resins prepared by the PDA method possessed higher initial thermo-oxidative stability than the BFBI/BMPM couple. However, 505°K cure was not sufficient to achieve high molecular weights necessary to take advantage of the high inherent stability achievable from the polymer structure. However, a similar poly(Diels-Alder) reaction was shown to be effective as a means to crosslink a polyphenylquinoxaline polymer.

Process improvements were identified for each approach in terms of prestaging necessary to achieve highly processable HMS prepreg tapes and subsequent autoclave cycles for the same. The modified processes were employed to prepare composite samples for detailed tests.

The final phase of the program consisted of determination of mechanical properties on composites prepared by the PMR and PDA approaches. Properties were determined before, during and after isothermal aging of specimens at 561°K (550°F) and 589°K (600°F) in air for 1000 hours. Retention of properties after the aging period gave strong evidence that both the PMR and PDA systems are suitable for autoclave fabrication of composites possessing useful long-term properties at 561°K. The 589°K properties were similar to those obtained on similar resin/composites in Contract NAS3-13489 which required significantly higher autoclave cure temperatures [561°K (550°F)] in previous work compared to 473°K to 505°K [(390°F to 450°F)] in the present studies.

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FIGURES (Continued)

I. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-15834, during the period of 1 May 1972 through 1 September 1973. This program consisted primarily of experimental studies structured to define low temperature [505°K (450°F)] low pressure [0.7 MN/m^2 (100 psi)] curing, autoclave addition-type polyimides. Although current studies were related to experimental work conducted previously in Contract NAS3-13489 (Reference 1) in terms of investigation of autoclavable pyrolytically polymerizable polymers, it was necessary to provide several innovative chemical and process modifications to meet the low temperature/pressure objectives of the current program. The autoclavable resins were intended for use to fabricate high performance graphite reinforced components for use in air breathing engine systems. The autoclavable resin matrices described herein were by concept and practice designed to offer high performance property retention for use during long-time durations in air at temperatures of 533°K (500°F) to 589°K (600°F).

The original concept investigated in this program concerned chemical modifications of end capped materials expected to undergo A-type or pyrolytic polymerization at temperatures within the maximum 505°K (450°F) cure temperature objective of this program. These end capped species were based on a norbornene-type alicyclic structure shown to be effective cure sites for P13N-type resins first examined under Contract NAS3-7949 (Reference 2) and later modified for specific NASA resin requirements in Contracts NAS3-12412, NAS3-13203 and NAS3-13489 (References 3, 4 and 1, respectively). As was previously demonstrated under NASA sponsorship (References 1 and 3), this resin system cures by a novel mechanism involving reverse Diels-Alder reactions of the prepolymer end cap structures, thus providing *in situ* formation of high performance polyimide macromolecules upon application of high temperatures and pressures [561°K to 589°K (550°F to 600°F) and 1.4 MN/m^2 to 7.0 MN/m^2 (200 psi to 1000 psi)]. New ingredient modifications other than those used originally in NAS3-7949, etc., were employed in initial autoclave studies (Reference 1) which imparted acceptable resin melt/flow/consolidation characteristics, but still required minimum cure temperatures of 561°K.

In the current work, it was found experimentally that eight norbornene-type end cap models could be prepared and made to undergo a prerequisite reverse Diels-Alder reaction at or near the maximum 505°K (450°F) cure temperature objective of the program. However, the constituents formed during the reverse Diels-Alder reactions would not copolymerize *in situ* similarly to that reaction undertaken by the simplest norbornene anhydride (nadic anhydride) as shown to be effective in Contract NAS3-12412 (Reference 3). Consequently, significant modification had to be made in the original conceptual approaches prior to eventual achievement of the autoclave goals of the program.

Once it was demonstrated that chemical structural modifications of nadic-type end caps would not yield to the desired integrity and 589°K initial thermo-oxidative stability, it was necessary to utilize two distinct and new technical approaches to meet program requirements. The first of the two approaches eventually utilized throughout the remainder of the program involved a NASA Lewis Research Center conceived process (Reference 5), in which addition-type cure of nadic containing compounds is effected by a process designated polymerization of monomeric reactants (PMR). Although preliminary evidence was available to show promise of 505°K (450°F) cure (Reference 6) of nadic-type end cap structures, it was necessary to define experimentally under what other parameters (e.g., pressure and time duration) that this low temperature cure became effective. Resin studies were concentrated on a 1500 g/mol formulated molecular weight version of prepolymer yielded by proper stoichiometric blending of nadic monomethyl ester (NE)/methylene dianiline (MDA)/benzophenone tetracarboxylic acid dimethyl ester (BTDE) shown to be very promising in previous NASA studies (Reference 5). Neat polymer processing studies established conditions for 505°K cure of this system and an appropriate range of variables were selected for composite fabrication as based on thermo-oxidative stability screening studies (samples possessing >589°K stability were deemed suitable for further work).

The second approach used to define resin candidates meeting gross program objectives was a novel polymerization/aromatization reaction sequence developed under independent research and development funds at TRW Systems (Reference 7). This approach is similar in nature to the PMR system, in that monomeric type ingredients are employed directly, but differs significantly in the polymerization method. The reaction route to polyimides consists of a poly(Diels-Alder) (PDA) addition-type condensation of bis(furan) capped imides and bis(dieneophiles). These ingredients polymerize at or near 473°K (400°F) to give initially an oxygen bridged six-membered ring which undergoes *in situ* thermal aromatization through loss of a mole of water to give aromatic polyimide structures. It was experimentally shown that a very versatile ingredient combination suitable for use in the program was bis(furfuryl) benzophenone tetracarboxylic imide (BFBI) and bis(4-maleimidophenyl) methane (BMPM) combined in a one to one stoichiometric mix. As was conducted for the PMR approach, processing variables were determined for the PDA system which were suitable for autoclave process investigations.

Engineering fabrication studies on promising PMR and PDA resins were initiated by conducting automatic dielectrometry (AUDREY) of effective cure temperatures as suggested by the neat resin studies. The initial AUDREY work employed style 181-type E-glass as the composite reinforcement material; during all remaining studies Hercules HMS graphite fiber was employed. The AUDREY results were used to structure matrices for definition of reasonable autoclave process cycles during which dimethyl formamide (DMF) was employed as the resin varnish solvent. It was shown during these initial studies that promise for fabrication of high performance composite panels at temperatures up to 505°K (450°F) existed for both resin systems and that postcure of composites at 589°K (600°F) yielded specimens demonstrating excellent retention of mechanical properties at 561°K.

Upon definition of suitable PMR and PDA resin candidates and processes for the same, additional studies were conducted to determine whether changes in solvent or ingredient modifications would significantly improve the processability, thermo-oxidative stability or mechanical property retention characteristics of the two autoclavable polymer approaches. In this study N-methylpyrrolidinone (NMP) was shown to offer certain advantages over DMF for effecting processing/property improvements. Preliminary evidence was gained that specific PDA ingredients which do not contain the labile methylene linkage in BFBI and BMPM could yield PDA polymers possessing very high thermo-oxidative stability (>589°K). During these studies, improvements for processing both PMR and PDA derived resin/composite candidates were discovered.

The final program activity consisted of detailed property evaluation, including long-term isothermal aging characterization, of HMS graphite reinforced composites prepared by the most promising process routes identified prior to initiation of this task. Mechanical properties and weight loss measurements conducted during and after isothermal aging of specimens from each system at 561°K (550°F) and 589°K (600°F) indicated that both resin system approaches show promise for preparation of high performance composites in an autoclave at temperatures up to 505°K (450°F) and pressures up to 0.7 MN/m^2 (100 psi) suitable for long term use in air at 561°K to 589°K. Considerable insight was gained into chemical and process modifications that are required to yield optimized representatives of both the PMR and PDA approaches.

During the program, attempts were made to adapt the furan derived Diels-Alder chemistry for effecting a facile polyphenylquinoxaline crosslink. In this brief study, a method to prepare bis(benzil) monomers possessing pendant crosslink sites was established. Significantly, use of the new furan capped bis(benzils) to prepare linear PPQ polymers by conventional synthesis techniques, followed by treatment with common bis(maleimides) yielded the highly desired crosslinked PPQ resin. Thus, a method was discovered for potential preparation of very high performance graphite reinforced composites in future studies.

This report is divided into five principal sections covering the program technical tasks: 1) (Task I) - Synthesis and Characterization of Pyrolytic End Caps, 2) (Task II) - Polymer Synthesis and Characterization, 3) (Task III) - Process Development and Evaluation, 4) (Task IV) - Resin Modification and Reproducibility and 5) (Task IV) - Final Composite Characterization. The significant conclusion reached from program studies are listed together with recommendations for activities that warrant further studies. This report also identifies new technology originating from the program in a separate section. The detailed information presented in the main body of this report is supplemented by Appendices covering procedures, characterization methodology and test equipment.

II. TASK I - MODEL STUDIES

The objective of this task was to identify suitable end cap structures which would allow addition-type pyrolytic polymerization cure of polyimide prepolymers in the temperature range of 477°K to 505°K (400°F to 450°F). A total of eight norbornene-type compounds were selected for study based upon experimental results and observations made in previous NASA supported programs.

The prime factor influencing selection of the new end cap candidates arose from the demonstration in Contract NAS3-13489 (Reference 1) that methyl nadic anhydride could be cured into useful resin products at lower temperatures than nadic anhydride investigated in detail in Contract NAS3-12412 (Reference 3). Consequently, it was deemed appropriate to study three other substituted nadic anhydride compounds. Also, because no previous studies had investigated norborneneamine-type end caps as potential candidates to yield high performance addition-type polymers, five compounds of this type were selected for study. Four of the five amino materials contained simple alkyl substituents (i.e., methyl) to once again assess the same potential means to lower temperature cure as was designed for the new anhydride counterparts.

The eight new endocyclic end cap candidates selected for study were prepared and characterized as simple imide model derivatives. Details of the Task I studies are presented below. Synthesis procedures and analytical data to substantiate proof of structure are given in Appendix A.

2.1 END CAP STRUCTURES SELECTED FOR STUDY

The eight endocyclic end cap structures selected for investigation as sites to achieve polymer cure at 477°K to 505°K (400°F to 450°F) were designated structures I to VIII and are shown on the following pages. The eight end caps were converted to their corresponding phthalimide or N-phenyl imide derivatives designated structures IX to XVI. The model imides were characterized and evaluated for potential to meet the maximum 505°K (450°F) cure objectives of the program. The synthesis, characterization and evaluation of compounds I to XVI are discussed in Sections 2.2 and 2.3.

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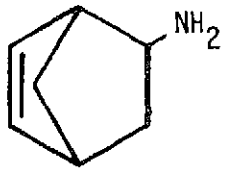
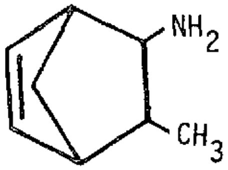


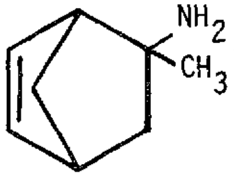
(I)

2-Amino-5-norbornene



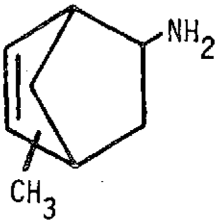
(II)

2-Amino-3-methyl-5-norbornene



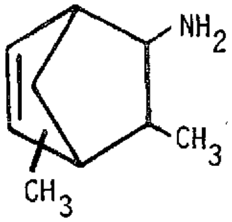
(III)

2-Amino-2-methyl-5-norbornene



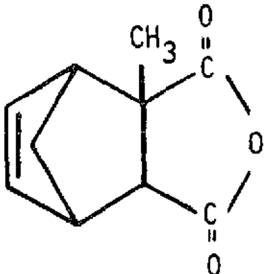
(IV)

2-Amino-x-methyl-5-norbornene



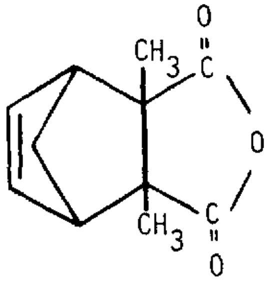
(V)

2-Amino-x,3-dimethyl-5-norbornene

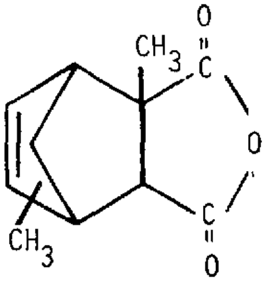


(VI)

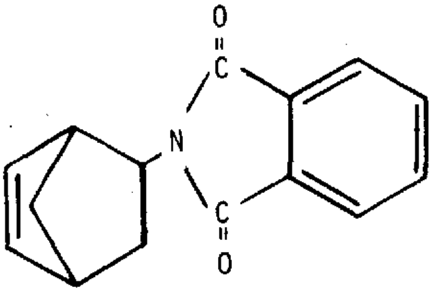
2-Methylnadic Anhydride



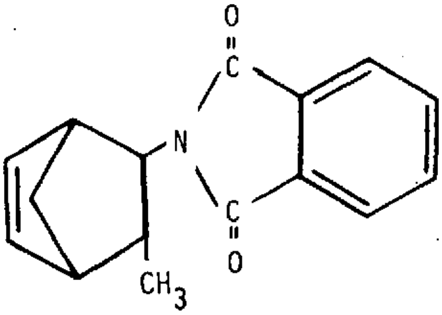
(VII)
2,3-Dimethylnadic Anhydride



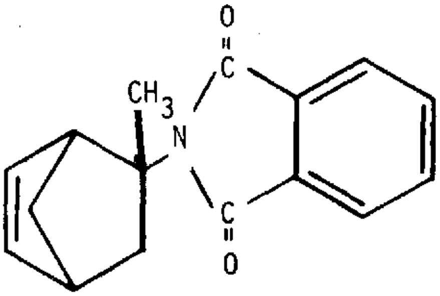
(VIII)
2,x-Dimethylnadic Anhydride



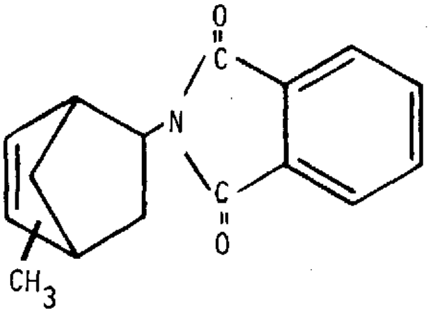
(IX)
2-Phthalimido-5-norbornene



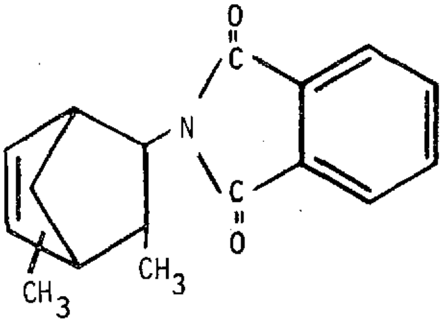
(X)
2-Phthalimido-3-methyl-5-norbornene



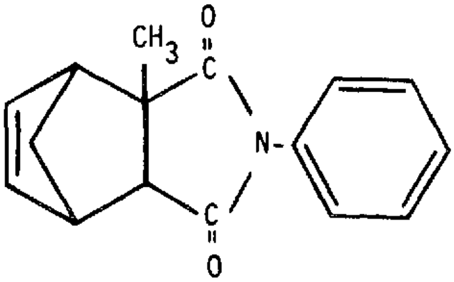
(XI)
2-Phthalimido-2-methyl-5-norbornene



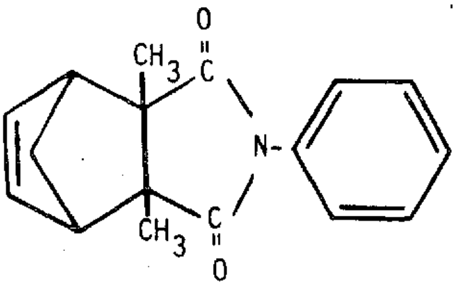
(XII)
2-Phthalimido-x-methyl-5-norbornene



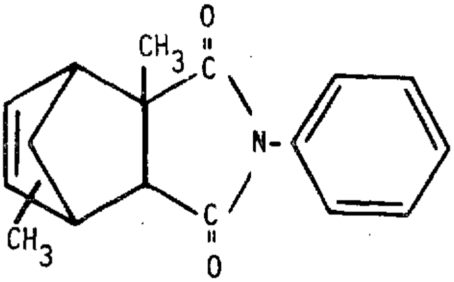
(XIII)
2-Phthalimido-x,3-dimethyl-5-norbornene



(XIV)
N-Phenyl-2-methylnadimide



(XV)
N-Phenyl-2,3-dimethylnadimide



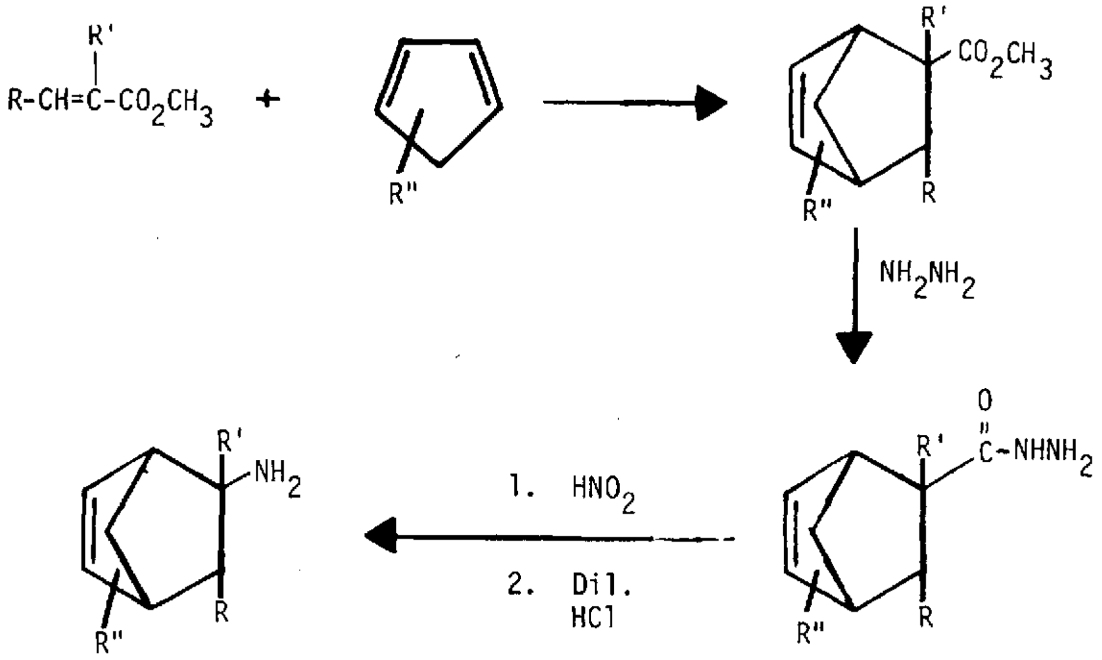
(XVI)
N-Phenyl-2,x-dimethylnadimide

2.2 SYNTHESIS OF END CAP AND MODEL IMIDE STRUCTURES

The synthesis of the eight endocyclic end caps selected for study and conversion to model imides was effected by established organic chemistry procedures. This work is described in the paragraphs below.

2.2.1 Synthesis of Amino Derivatives

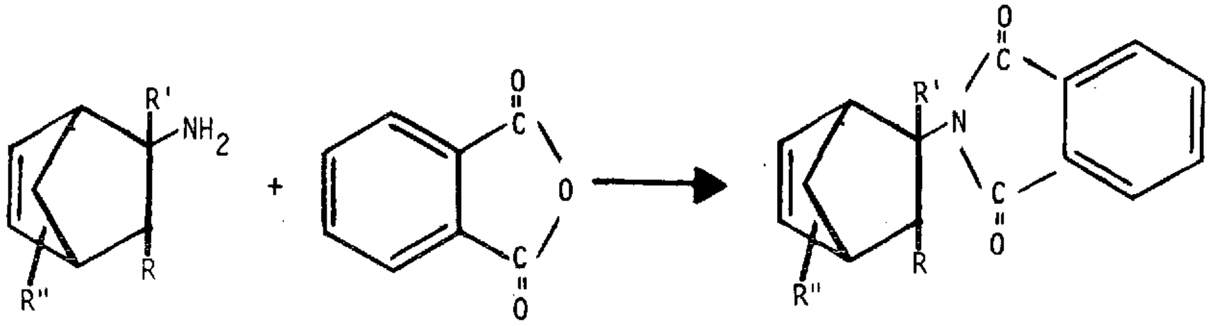
Synthesis of the endocyclic amine structures (I-V) given in Section 2.1 was accomplished by the Curtius rearrangement (Reference 8) as follows:



where R, R' and R" = H or CH_3 to give structures I-V.

The yields obtained for each of the amines are summarized in Table I. The results indicate that methyl groups substituted on the second or third carbon atom, which includes structures II, III and V, materially reduces the yield of desired product when compared with structures I and IV which are not substituted in the second or third carbon atom. This reduction of yield on the methyl substituted compounds is most probably due to steric hindrance by the methyl group. No attempt was made to optimize yields for any of the five amino compounds. The procedure employed to prepare the compounds and methods employed to establish correct structure are given in Appendix A.

The five amino derivatives were converted to their corresponding phthalimide derivatives (Structures IX to XIII, respectively) by a simple one-step reaction with phthalic anhydride as shown on the following page. Representative procedures employed to prepare 2-phthalimido-5-norbornene (IX) are presented in Appendix A along with structure characterization results obtained on the model imide structures. Other analyses pertinent to



where R, R', and R" = H or CH_3 to give structures IX to XIII.

establishment of minimum reverse Diels-Alder behavior are described in Section 2.2.3.

TABLE I

SUMMARY OF ENDOCYCLIC AMINE SYNTHESIS RESULTS[a]

Amino[b] Compound	Yield in Curtius Reaction Sequence Ester	Hydrazide	Amine	Qualitative Estimation of Synthesis
I	76%	76%	36%	Acceptable
II	30%	22%	5%	Inferior
III	10%	5%	1%	Inferior
IV	c	c	33%	Acceptable
V	43%	39%	10%	Inferior

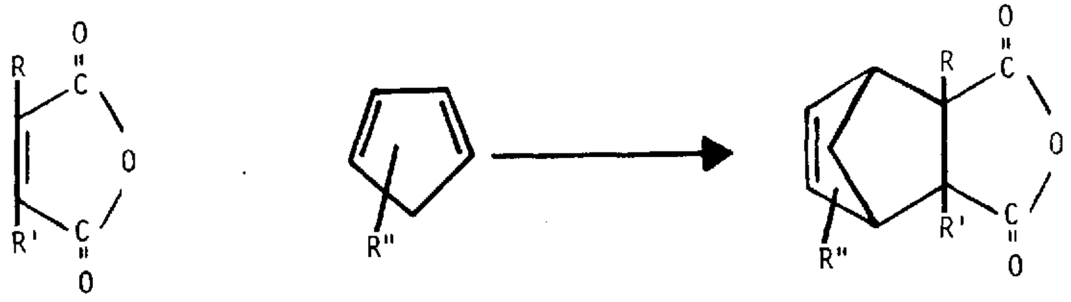
[a] According to Curtius reaction scheme given on Page 11

[b] For names and structure see Section 2.1

[c] Intermediates were not isolated

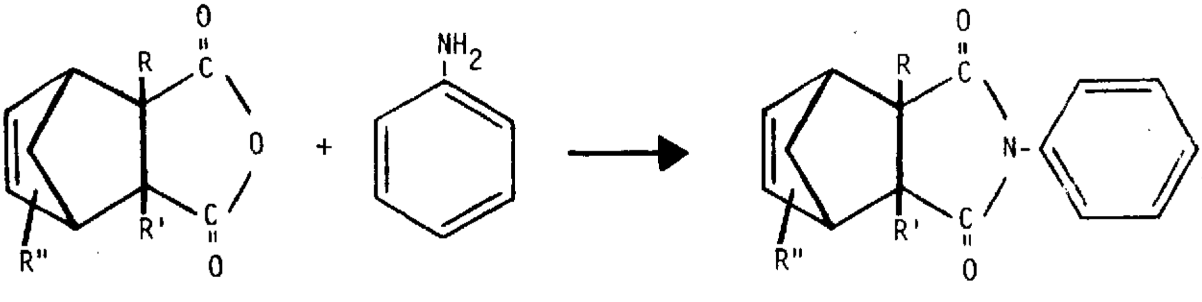
2.2.2 Synthesis of Anhydride Derivatives

The three endocyclic anhydride structures given in Section 2.1 (VI-VIII) were prepared by the simple Diels-Alder addition shown below:



where R, R', and R" = H or CH_3 to give structures VI-VIII.

The anhydrides so prepared, were converted to N-phenyl imides (Structures XIV to XVI) by a one-step reaction with aniline by the well-established chemistry used for nadic anhydride in Contract NAS3-12412 (Reference 3) as shown below:



where R, R' and R" = H or CH_3 to give structures XIV to XVI.

Representative experimental procedures used to prepare 2-methyl nadic anhydride (VI) and N-phenyl-2-methyl nadimide (XIV) are described in Appendix A along with structure characterization results. Other key characterization of the model imides is described in Section 2.2.3.

2.2.3 Characterization of the Thermal Behavior of Model Imides

Each model imide was subjected to analyses designed to provide information on reverse Diels-Alder behavior. Details of these studies are provided below.

2.2.3.1 Differential Scanning Calorimetry Analysis (DSC) - The thermal behavior of each model imide was assessed by DSC analysis. It was originally planned to employ DSC for obtaining both a melting point and a minimum reverse Diels-Alder temperature (MRDAT) for each model imide (compounds IX to XVI). However, as can be seen from the results of DSC analysis in Table II, the amount of information gained from this study was minimal.

TABLE II
DIFFERENTIAL SCANNING CALORIMETRY MELTING POINTS

Model Imide Structure[a]	DSC Melting Point [°K (°F)]	Apparent MRDAT [°K (°F)]
IX	368-370 (203-207)	585 (594)
X	b	c
XI	b	c
XII	b	c
XIII	b	c
XIV	376-378 (217-221)	545 (520)
XV	328-331 (131-136)	c
XVI	b	c

[a] For structures see Section 2.1.2

[b] DSC melting point not discernible; imide is a semi-solid at room temperature

[c] Sample apparently sublimed at approximately 473°K

Four of the model imides (i.e., structures IX, XI, XIV and XV) were crystalline solids and melting points were easily obtained. However, only two of these four imides, IX and XIV, gave a discernible MRDAT as clearly appearing in the DSC scan as an exotherm. In the case of compounds XI and XV, as well as for semi-solid compounds X, XII, XIII and XVI, the non-appearance of an exotherm attributable to a MRDAT apparently is due to sublimation of the model imides at temperatures of approximately 473°K (392°F) at ambient pressure.

The semi-solid state of model imide structures X, XII, XIII and XVI is not that unusual, since each of these four compounds has a methyl substituent on the endocyclic ring, located in a position other than the juncture carbon atom(s) of the amine or anhydride group. A simpler analogy is well-known in this respect; methyl nadic anhydride is a high boiling liquid whereas nadic anhydride is a crystalline solid (References 1 and 3).

Attempts were also made to discern an approximate MRDAT value for the eight model imides by TGA experimentation. The results of this study are presented in the following discussion.

2.2.3.2 Thermogravimetric Analysis (TGA) - The model imides were subjected to TGA screening in air to attempt definition of a minimum reverse Diels-Alder temperature (MRDAT). The results of the TGA analysis are shown in Table III and shed some additional light on an approximate MRDAT.

TABLE III
THERMOGRAVIMETRIC SCREENING OF MODEL IMIDES

Model Imide[a] Structure	Temperature at which First[b] Weight Loss Break Occurred [°K (°F)]	Inflection Temperature [°K (°F)]
IX	410 (278)	481 (408)
X	473 (392)	508 (454)
XI	461 (370)	493 (428)
XII	473 (392)	503 (446)
XIII	473 (392)	523 (482)
XIV	436 (323)	492 (425)
XV	473 (392)	498 (437)
XVI	436 (323)	485 (413)

[a] For structures see Section 2.1.2

[b] Scanned at 3°K/min rate; flow = 100 cc/min

Past studies in Contracts NAS3-12412 and NAS3-13489 (References 3 and 1) have shown that an inflection point in the TGA of model imides closely parallels the MRDAT of that compound and frequently occurs near the minimum cure temperature for the end cap from which the model imide was prepared. The TGA inflection point MRDAT's of <505°K (450°F) for model imide structures indicated potential for achievement of low temperature cure.

The MRDAT values determined by DSC and TGA, if discernable, were used to establish a minimum effective cure temperature in pyrolysis studies as presented in Section 2.3.

2.3 PYROLYSIS STUDIES

The evaluation of model imide structures IX through XVI to achieve a minimum reverse Diels-Alder temperature to meet program autoclavability objectives is presented in the following sections.

2.3.1 Pyrolysis Studies

Pyrolysis studies on model imide structures IX to XVI were conducted employing the same apparatus and methodology utilized in Contract NAS3-13489 (Reference 1). A schematic representation of the apparatus employed is given in Figure 1. The study employed fixed experimental parameters, including temperatures near the minimum reverse Diels-Alder temperature (MRDAT) established by DSC and/or TGA (see Section 2.2).

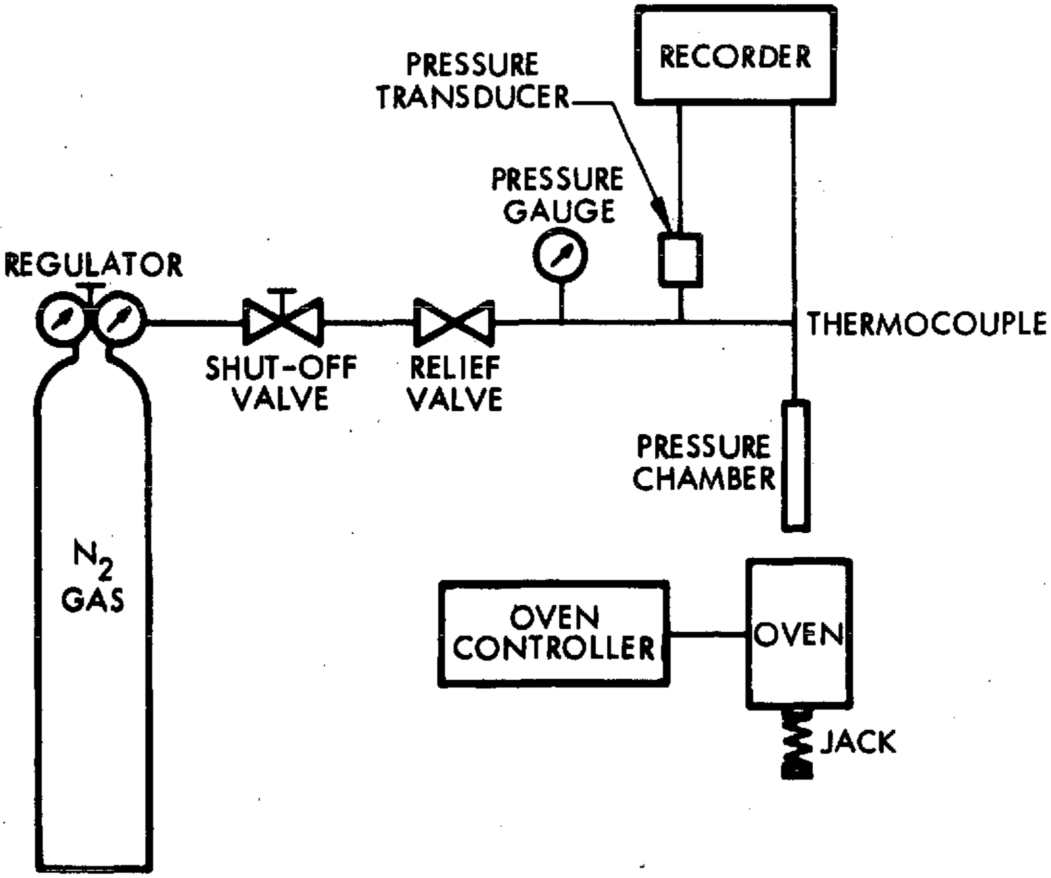


Figure 1. Schematic of Pressure Pyrolysis Experimentation Set-up

Initial pyrolysis studies were conducted on model imide structure XIV, N-phenyl-2-methylnadimide, because of promising MRDAT characterization results obtained as described in Section 2.2. A promising pyrolytic polymerization catalyst, tin tetrachloride ($SnCl_4$), discovered in Contract NAS3-13489 (Reference 1) was employed throughout the pyrolysis studies.

As can be seen from the results of experimentation performed on model imide XIV presented in Table IV, a cure temperature of 533°K (500°F) gave a pyrolysis residue of acceptable initial thermo-oxidative stability of 589°K (600°F) indicative of high performance polymer attainment. Although 533°K was above the desired maximum cure temperature of 505°K (450°F), it still marked a significant reduction of the 561°K (550°F) minimum cure temperature established for an end cap derived from methyl nadic anhydride. As a result of screening studies conducted on compound XIV, the following pyrolysis variables were fixed for evaluation of the remaining model imides.

- A fixed pressure of 1.4 MN/m^2 (200 psig),
- A tin tetrachloride ($SnCl_4$) catalyst level of 3% w/w,
- A pyrolysis temperature of 533°K (500°F) and
- A four-hour pyrolysis duration.

The complete results of model imide pyrolyses according to the fixed parameters given above are presented in Table IV. As can be seen from these results, only model imide structure XIV, prepared from end cap candidate 2-methylnadic anhydride (VI), gave an indication of promise to yield a thermo-oxidatively stable polymer at 533°K (500°F). The results were disappointing in view of the tendency of each of the eight end caps to undergo reverse Diels-Alder near the 505°K (450°F) temperature objective of the program.

The experimental results all led to one conclusion, specifically that the active species formed from structures IX through XVI during pyrolysis do not recombine at temperatures below 533°K (500°F) to give a useful polymer structure under the conditions studied. Extensive studies conducted in earlier efforts (References 1 and 3) concentrated on pyrolysis at 589°K

Table IV

SUMMARY OF PYROLYSIS EXPERIMENTATION[a]

Model Imide Structure[b]	Variables Employed			Initial TGA Weight Loss[c] (°K/°F)
	Temperature (°K/°F)	$SnCl_4$ Catalyst Level (w/w %)	Pyrolysis Duration (Hours)	
IX	505/450	1	1	d
	533/500	3	4	516/470
X	533/500	3	4	423/302
XI	533/500	3	4	433/320
XII	533/500	3	4	428/312
XIII	533/500	3	4	433/320
XIV	505/450	1	1	d
	505/450	5	4	516/470
	533/500	1	1	422/300
	533/500	1	4	500/440
	533/500	3	4	589/600
	533/500	5	2	572/570
XV	533/500	3	4	473/392
XVI	533/500	3	4	453/358

[a] All pyrolyses performed at 1.4 MN/m^2 (200 psi)

[b] See Section 2.1.2

[c] TGA scan rate = 3°K/min and 100 ml/min flow (air)

[d] Semi-solid residue obtained - unsuitable for test

(600°F), which was shown to be the most facile cure temperature for polymers prepared from pyromellitic dianhydride (PMDA) and end capped with nadic anhydride (NA) and methyl nadic anhydride (MN). As a result of the pyrolysis studies conducted on eight logical alternative end cap variations (I to VIII), it was obvious that structures possessing a substituted norbornene ring would not directly yield polymers employing cure temperature of ≤505°K (450°F) that are stable to 561°K to 589°K (550°F to 600°F) in air.

However, additional screening studies conducted at the conclusion of Task I led to definition of suitable methods to achieve the goal autoclave cure. These highly significant investigations are presented below.

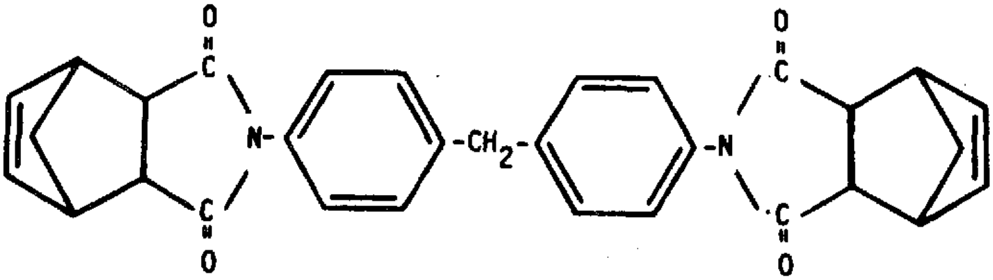
2.4 ADDITIONAL MODEL REACTION STUDIES

At the conclusion of the Task I studies on candidate end cap compounds I to VIII, it was decided to investigate two other potential routes to achieve the goal 505°K (450°F) cure temperature. The highly significant studies which led to definition of two very promising autoclavable addition-type polyimides are described in the paragraphs below.

2.4.1 Additional Pyrolysis Studies Employing the End Capped Approach

During discussions on the results of the pyrolysis studies described in Section 2.3, a disclosure was made that independent studies at NASA/Lewis Research Center (Reference 6) showed some potential for cure of the well characterized nadic anhydride end cap species (Reference 3) at or near 505°K. Consequently, it was decided to investigate a bis(imide) model prepared from nadic anhydride.

The model compound selected for study was bis(4-nadimidophenyl) methane (BNPM) shown as structure XVII below. Details of the preparation of BNPM are given in Appendix A.



BNPM

A study was conducted as summarized below:

- Prepare model imide BNPM (XVII); characterize by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.
- Conduct pyrolyses of BNPM employing temperatures of 505°K (450°F), 513°K (475°F) and 547°K (525°F), a pressure of 1.4 MN/m^2 (200 psi) and a time duration of four hours.
- Determine initial thermo-oxidative stability (TOS) of the three pyrolysis residues by TGA analysis in air and a quantitative weight balance of pyrolysis product vs. model imide.
- Postcure each pyrolysis residue under nitrogen employing a linear heat-up rate from 477°K (400°F) to 589°K (600°F), followed by a two-hour isothermal cycle at 589°K (600°F).
- Repeat TGA and weight balance determinations on postcured specimens.

The results of the study on BNPM are summarized in Table V. As can be seen from the data, all samples yielded polymers of high initial TOS after postcure. The low resin weight loss after both cure and postcure,

TABLE V

SUMMARY OF PROPERTIES DETERMINED ON BNPM

Pyrolysis Temperature (°K/°F)	Weight Loss Break in TGA Curve (°K/°F)		Measured Weight Loss of Sample (%)	
	Initial Cure	Postcured[b]	Cured	Postcured
505/450	543/518(1st) 653/716(2nd)	633/680(only)	0.5	0.4
519/475	373/212(1st) 648/707(2nd)	608/635(only)	0.4	0.5
547/525	598/617(only)	573/572(only)	0.5	0.8

a. Other conditions: 1.4 MN/m^2 (200 psi) and 4 hour duration

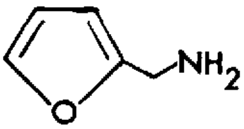
b. Postcure cycle consisted of 4 hour linear heat-up rate from 477°K (400°F) to 589°K (600°F), followed by 2 hour isothermal cycle at 589°K (600°F) (all in a nitrogen environment)

c. Scan rate of 3°K/min and air flow of 100 ml/min coupled with the high TOS, strongly suggested that cyclopentadiene evolved during pyrolytic cure (References 1 and 3) is effectively incorporated into the polymer structure.

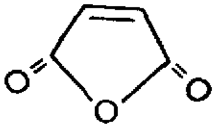
The results of this study were deemed highly significant and a set of specific ingredients were selected for investigation of this approach in Tasks II and III.

2.4.2 Poly(Diels-Alder) Approach

Another addition-type reaction of potential promise to meet the current program objectives consists of poly(Diels-Alder) chemistry. During 1970 and 1971, TRW Systems investigated a novel form of Diels-Alder chemistry on Independent Research and Development funds (Reference 7). These studies proved the feasibility of preparing stable aromatic polyimides from the simultaneous Diels-Alder/condensation reaction of furfuryl amine (FFA) and maleic anhydride (MA) shown below.

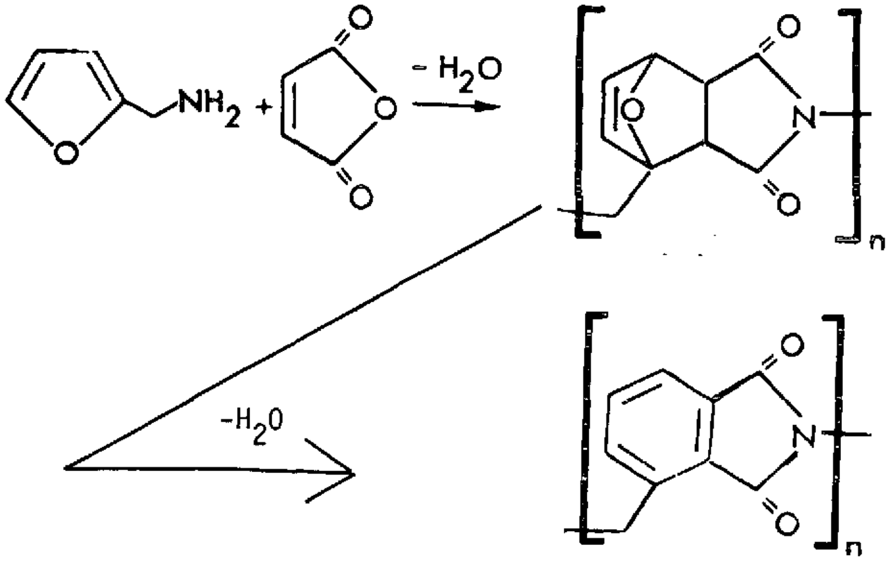


Furfuryl Amine (FFA)



Maleic Anhydride (MA)

It was shown that a simple stoichiometric mixture of FFA and MA could be melt polymerized to give a poly(endoxy) structure which could be aromatized *in situ* to give an aromatic polyimide according to the reactions (1) and (2) on the following page. It was thought that a similar difunctional approach might be applicable to the current program. Consequently, two stable bis(reactants), bis(2-furfuryl) pyromellitimide (BFPI) and bis(4-maleimidophenyl) methane (BMPM), were prepared and polymerized.



(1)

(2)

Promise for the PDA reaction was shown by heating a mixture of the BFPI and BMPM ingredients in the TGA under flowing nitrogen (100 ml/min) from 298°K (75°F) to 589°K (600°F), at a heating rate of 3°K/min (5.5°F/min). The thermogram is shown in Figure 2, where one can see the sample does lose weight gradually to 589°K. When the polymer residue obtained from the TGA in nitrogen was rerun at the same conditions in air, no weight loss occurred until the temperature reached 630°K (640°F). This indicated that in approximately one and one-half hours a stable polymer is produced.

Evidently, the BFPI and BMPM monomers also react to give a polymer of the gross oxygen bridged structure shown in Equation 3 which appears to undergo dehydration, *in situ*, to the aromatic structure shown in Equation 4). The dehydration of polymer A to polymer B evidently occurred gradually during polymerization at or near 505°K (450°F).

The promise of the poly(Diels-Alder) reaction was held to be sufficient to assess this approach in detail to produce autoclave processable polymers concurrently with the pyrolytic approach discussed in Section 2.4 in Task II.

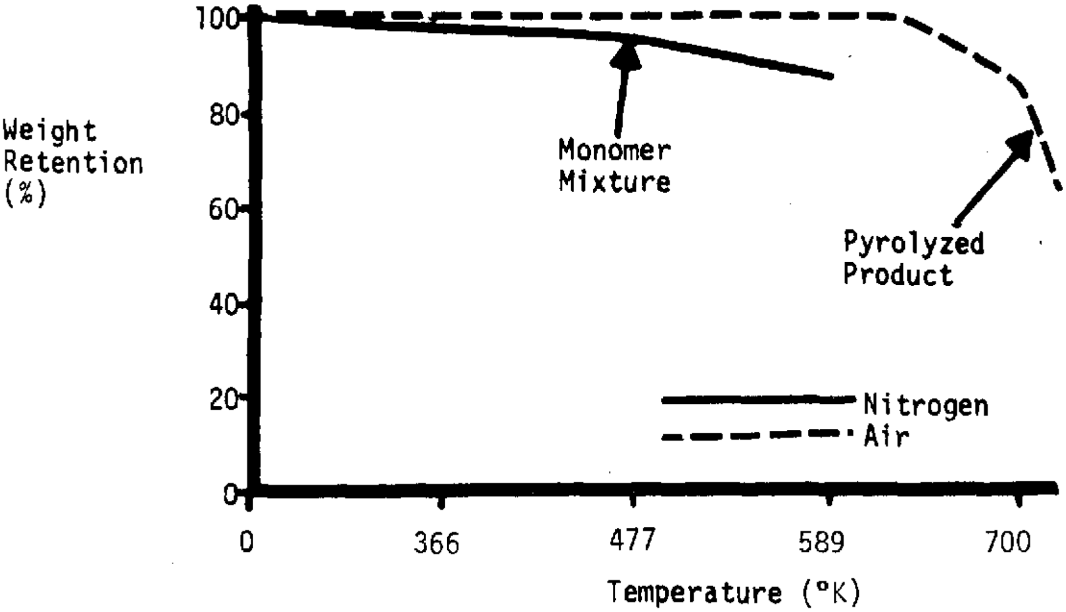
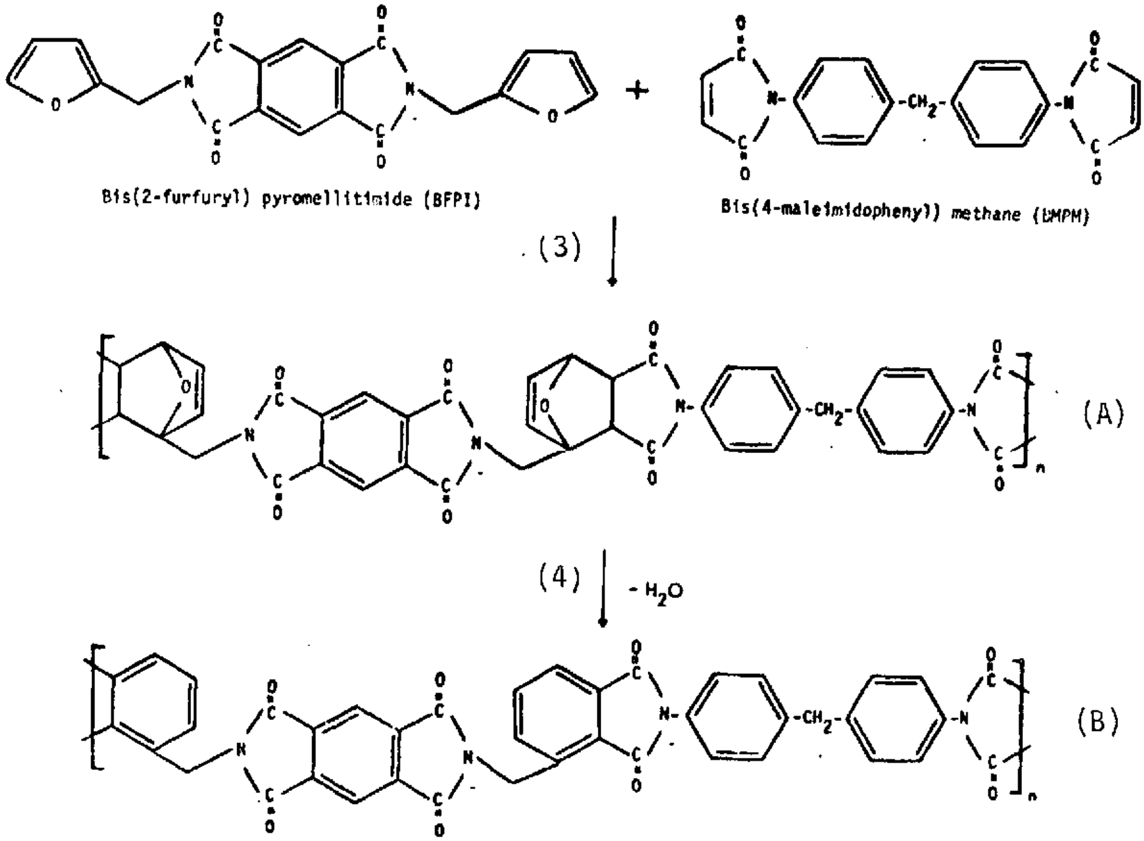


Figure 2. Thermograms of Monomer Mixture and Pyrolyzed Product (Scan Rate = 3.0°K/min; flow = 100 ml/min)



III. TASK II - POLYMER STUDIES

The objective of this task was to utilize the findings of Task I to prepare candidate autoclavable resins and screen them for physical, chemical and thermo-oxidative properties. The results obtained in Task I indicated that two promising approaches had been identified for accomplishing the autoclavable cure objectives on the program. These two approaches, namely the pyrolytic end cap and the poly(Diels-Alder) approaches, were used to prepare neat resin samples which were subsequently screened for potential to meet program objectives. Investigations were then conducted on the processing characteristics of the neat resin systems to aid subsequent composite fabrication studies.

In the Task II studies, the poly(Diels-Alder) (PDA) approach was screened in detail to establish the potential of the novel reaction to achieve the low temperature ($\leq$505°K) autoclave processability objectives of the program. Details of this study are presented in Section 3.1. Parallel assessment of the PDA route with the pyrolytic end cap approach is presented in Section 3.2.

3.1 POLY(DIELS-ALDER) SCREENING STUDIES

The results obtained in Task I studies indicated that the bis(furfuryl) pyromellitimide/bis(4-maleimidophenyl) methane (BFPI/BMPM) mixture upon polymerization gave a residue that showed high promise of meeting the program objectives (see Section 2.4.2). To further characterize this system, an investigation of various cure conditions and the effect of postcure on the resulting polymer samples was performed. The polymerizations were run in the melt, employing an apparatus identical to that used for the model imide pyrolyses as described in Section 2.3.

Eight polymerization runs were conducted employing temperatures of 477°K (400°F) and 505°K (450°F), pressures of 1.33×10^{-5} N/m^2 (1 Torr) vacuum and 1.4 MN/m^2 (200 psi) and time durations of 2 hours and 4 hours. Each residue was then postcured in vacuum employing a 4 hour linear heat-up cycle from 477°K (400°F) to 589°K (600°F), followed by a 2 hour isothermal cycle at 589°K. For the sake of simplicity, a short hand notation will be employed to describe each sample. The notation to be employed is as follows:

- Polymers prepared from BFPI and BMPM are designated XVIII.
- Temperatures are given as 477 for 477°K and 505 for 505°K.
- Pressures are designated at V for 1.3×10^{-5} N/m^2 (vacuum) and P for 1.4 MN/m^2.
- Time durations are shown as 2 for 2 hours and 4 for 4 hours.
- Postcured samples are designated with a PC.

Using this coding, the sample of BFPI and BMPM polymerized at 477°K under 1.33×10^{-5} N/m^2 vacuum for two hours is described as XVIII-477-V-2 and the same sample after postcure is shown as XVIII-477-V-2-PC. This notation scheme is summarized in Table VI.

Each polymerization residue obtained in this study was a well consolidated plug, indicating total melt occurred in all polymerizations. The eight samples obtained according to the experimentation given in Table VI were powdered prior to analysis and/or postcure. Any volatile matter content evolved during the polymerization and postcure was trapped and analyzed by mass spectroscopy.

3.2 ANALYSIS OF BFPI/BMPM POLYMER SCREENING SAMPLES

Each of the sixteen polymer residues obtained from the cure and postcure experimentation summarized in Table VI was analyzed by thermogravimetric (TGA) and infrared (ir) analysis. The effluents from the eight polymerization runs and the collective postcure run were collected and analyzed by mass spectroscopy (MS) and weight retention of the polymer residue during cure and postcure was also measured.

3.2.1 Analysis of Cured Samples

The results of analyses performed on cured samples are presented in Table VII. These results illustrate several characteristics of the poly(Diels-Alder) polymer structure. During the cure cycle, very little (ca. 2%) weight loss occurred indicating that some of the postulated *in situ* aromatization does take place. This observation is supported by the

TABLE VI

SUMMARY OF POLYMERIZATION PARAMETERS EMPLOYED TO SCREEN BFPI/BMPM RESIN COMBINATION

Sample Designation	Polymerization Parameters Studied						
	Temperatures		Pressures		Durations		Postcure[a]
	477°K (400°F)	505°K (450°F)	1.33 x 10^{-5} N/m^2 (vacuum)	1.4 MN/m^2 (200 psig)	2 hours	4 hours	
XVIII-477-V-2	X		X		X		
XVIII-477-V-2-PC	X		X		X		X
XVIII-447-V-4	X		X			X	
XVIII-477-V-4-PC	X		X			X	X
XVIII-477-P-2	X			X	X		
XVIII-477-P-2-PC	X			X	X		X
XVIII-477-P-4	X			X		X	
XVIII-477-P-4-PC	X			X		X	X
XVIII-505-V-2		X	X		X		
XVIII-505-V-2-PC		X	X		X		X
XVIII-505-V-4		X	X			X	
XVIII-505-V-4-PC		X	X			X	X
XVIII-505-P-2		X		X	X		
XVIII-505-P-2-PC		X		X	X		X
XVIII-505-P-4		X		X		X	
XVIII-505-P-4-PC		X		X		X	X

[a] All samples were postcured at one time employing a 4 hour linear heat-up rate from 477°K to 589°K, followed by a 2 hour isothermal cycle at 589°K under a constant 1.33 x 10^{-5} N/m^2 vacuum.

TABLE VII

RESULTS OF ANALYSES CONDUCTED ON CURED BFPI/BMPM POLYMERIC RESIDUES

Sample Designation[a]	Percent Sample Recovered After Cure (%)[b]	TGA Screening Temperature at Which First Major Break Occured in Curve (°K/°F)[c]	Weight Loss Up To Major Break (%)
XVIII-477-V-2	99.4	598/617	4
XVIII-477-V-4	99.0	598/617	5
XVIII-505-V-2	98.2	510/458 (1st); 623/662 (2nd)	7
XVIII-505-V-4	98.0	573/572 (1st); 623/662 (2nd)	14
XVIII-477-P-2	99.8	583/590	8
XVIII-477-P-4	99.9	463/374 (1st); 623/662 (2nd)	11
XVIII-505-P-2	99.8	598/617	12
XVIII-505-P-4	99.8	585/594	6

a. See Table VI for code explanation.

b. Determined by weighing test tube containing the sample before and after the polymer run.

c. TGA runs were made at a scan rate of 3°K/min employing and air flow rate of 100 ml/min.

fact that the MS scan of the effluent for each sample did show water to be present. The TGA results showed the PDA derived resins to have a final decomposition break at temperatures up to approximately 583°K (590°F). Further information was also gained from the shape of the TGA curve. There was a gradual loss of weight above 423°K (302°F) until the final decomposition occurred. This result was attributed to the occurrence of the postulated *in situ* aromatization up to final decomposition temperature and suggested that postcuring the residue would promote the *in situ* aromatization and yield a fully cured resin, thereby increasing the final decomposition temperature.

3.2.2 Analysis of Postcured Samples

The postcured samples, processed by employing a 4 hour linear heat-up rate from 477°K to 589°K followed by a 2 hour isothermal cycle at 589°K under a constant 1.33×10^{-5} N/m^2 vacuum, as summarized in Table VI, were characterized by the methods employed for their cured predecessors. These results are summarized in Table VIII.

As can be seen from the data in Table VIII, each sample lost 12% to 15% w/w on postcure. Some weight loss of the cured samples was expected based on the TGA results which showed losses of up to 14% w/w before a major break. The combined effluents of the samples generated during postcure were collected and analyzed by MS. The major portion was found to be water, thus supporting the occurrence of the postulated *in situ* aromatization during postcure. However, the amount of trapped volatile matter from the postcure accounted for a maximum of eight percent of the observed weight loss. The remainder of the weight loss was caused by the formation of a sublimate during the postcure. Infrared analysis showed the sublimate to be BFPI, indicating incomplete reaction with the bis(maleimide). Even though the PDA reaction was incomplete, the TGA results for the postcured samples shown in Table VIII show a significant improvement in initial TOS. Two samples, XVIII-477-P-2-PC and XVIII-505-P-2-PC demonstrated a postcure initial TOS of 623°K (662°F).

The results of the cure and postcure studies were assessed and cure conditions were selected for use in future PDA studies. The reaction

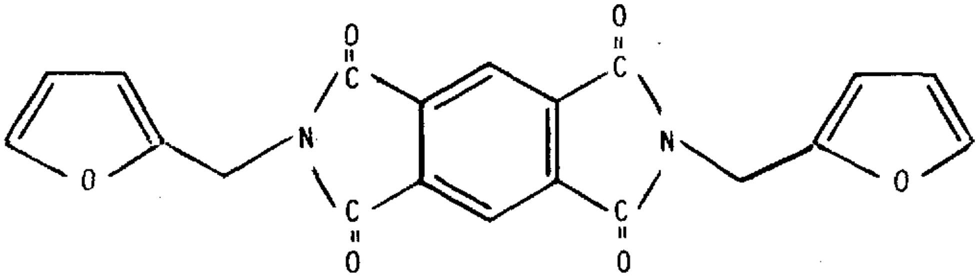
TABLE VIII

RESULTS OF ANALYSES CONDUCTED ON POSTCURED BFPI/BMPM POLYMERIC RESIDUES

Sample Designation[a]	Percent Sample Recovered After Postcure (%)	TGA Screening as Temperature at Which First Major Break Occurred in Curve ($^\circ$K/$^\circ$F)[b]
XVIII-477-V-2-PC	88	583/590
XVIII-477-V-4-PC	88	598/617
XVIII-505-V-2-PC	89	598/617
XVIII-505-V-4-PC	89	583/590
XVIII-477-P-2-PC	86	623/662
XVIII-477-P-4-PC	85	593/608
XVIII-505-P-2-PC	88	623/662
XVIII-505-P-4-PC	89	578/581

a. See Table VI for explanation of code

b. TGA runs were made at a scan rate of 3°K/min employing an air flow rate of 100 ml/min.

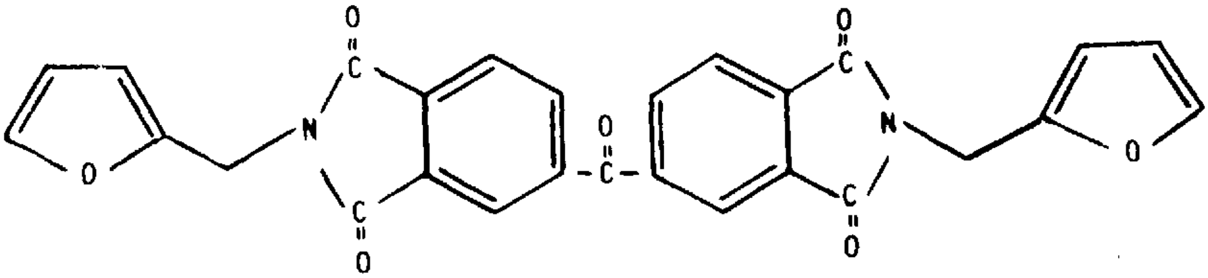


BFPI

conditions were consistent with program objectives and included were 505°K (450°F) temperature, 1.4 MN/m^2 (200 psi) pressure and two hour duration. These conditions were selected, in addition to near goal process conditions, because the sample obtained possessed higher initial TOS on cure and less weight loss on postcure.

Infrared analysis of the postcured residues was also performed. Each spectrum showed imide absorption at 1720 cm^{-1} to 1730 cm^{-1} and 1780 cm^{-1} to 1790 cm^{-1}. The downfield bands in the spectrum are less pronounced for the postcured sample as compared to the cured sample, thus indicating further polymerization had occurred. Spectra are provided in Appendix B along with descriptions of the cure/postcure procedures.

At the conclusion of the PDA reaction screening study it was shown that a new bis(furan) imide, bis(2-furfuryl) benzophenone tetracarboxylic imide (BFBI), also gave promising polymer results on cure at 477°K (400°F).



BFBI

In addition, the BFBI gave no sublimate on postcure, indicating it to be a more suitable monomer for reaction with BMPM. For these reasons, the BFBI/BMPM reactants were selected for all further Task II studies on the PDA reaction.

3.3 DETAILED POLYMER PROCESS STUDIES

Because the PDA approach showed promise to achieve program objectives, processing studies were conducted on both the PDA reaction and the nadic approach (see Section 2.4.1). The process studies are discussed in detail in the following paragraphs.

As was stated in Section 3.2, the BFBI/BMPM ingredient combination was selected for additional study on the PDA approach. The polymerization of monomeric reactants (PMR) approach discovered at NASA/Lewis Research Center (Reference 5) was used to prepare nadic end-capped pyrolytic curing polymers. The monomeric combination selected for study was a mixture of nadic monomethyl ester (NE), benzophenone tetracarboxylic acid dimethyl ester (BTDE) and methylene dianiline (MDA) at a stoichiometry to yield 1500 g/mol formulated molecular weight (FMW) prepolymer. This formulation was previously shown to have high promise in composites fabricated by press methodology (Reference 5).

In order to provide additional neat resin information on the PMR and PDA approaches, a three part study was conducted to yield preliminary data for aiding composite fabrication studies. These studies consisted of:

- Precure of monomer mixture to develop structural/chemical data relevant to imidization or resin advancement during simulated prepreg operations.
- Cure studies to develop structural/chemical data under simulated autoclave cycle conditions, and
- Postcure studies to develop structural/chemical information indicating whether a postcure cycle in an oven after autoclave fabrication is desirable or necessary.

The results of these studies on each of the three distinct processing steps are presented below.

3.3.1 Precure Studies

A study was conducted to determine the effect of temperature and time parameters on physical properties of the PMR and PDA resin candidates during precure. The samples were heated at atmospheric pressure under a nitrogen atmosphere for the times and temperatures given in Figure 3.

Each sample was then characterized by the following methods:

- Infrared analysis to determine amide/imide formation (PMR approach) and change in fine structure (PDA approach) indicative of prepolymerization.
- Boil in DMF at 20% w/w solids loading to study imidization or resin advancement (i.e., imidized or polymerized resin should be insoluble under these conditions).
- Melting point on a Fisher/Johns apparatus to discern melt/flow characteristics required for processing (autoclave cure).

Temperature of Staging (°K/°F)	Time of Staging (Hrs)				
	1	2	4	8	24
394/250			X	X	X
422/300			X	X	X
450/350		X	X	X	
477/400	X	X	X		

Figure 3. Precure Matrix

The results obtained on the PMR approach (Table IX) show that under even mild precure conditions the prepolymer obtained is substantially imidized and does not completely melt, flow and consolidate when reheated to 505°K (450°F). All the precured samples behaved similarly in that no melting point occurred up to 505°K and all demonstrated very low (0-5% w/w) solubility in DMF. The imide formation was confirmed by infrared analysis. The carbonyl band was also observed to be stronger in the samples heated at 477°K (400°F).

The measured weight losses of the resin samples during precure are also informative. The theoretical weight loss to give a fully imidized prepolymer (1500 FMW) is ca. 17% w/w of the monomeric starting ingredients. The observed weight loss (17% w/w) for the samples heated at 422°K for twenty-four hours and for one hour at 477°K would infer that imidization is complete under these conditions which is also supported by the IR analysis.

The results for the PMR resin sample NE/MDA/BTDE (1500 FMW) strongly suggested that prereaction was unsuitable for completion of the neat resin studies. Consequently, the monomeric ingredients were heated directly with any precure at 505°K to conduct cure and postcure studies.

Different behavior was observed for the prestaging of BMPM and BFBI ingredients selected for the PDA resin approach. The results of this study using the identical reaction parameters and analyses employed for the PMR approach are also given in Table IX.

As can be seen from the data, a significant rate of Diels-Alder reaction apparently does not occur until the BFBI/BMPM ingredients are heated to >450°K (350°F). This is indicated by the remelting and solubility characteristics of resin samples staged at 394°K (250°F), 422°K (300°F) and 450°K (350°F). These staged samples were observed to be melt processable when reheated at 505°K.

Infrared analyses of the staged PDA resin did not indicate any substantial change in structure under the conditions studied. The weight loss measurements performed on each sample indicate that a trend towards greater weight loss occurs as the staging temperatures is raised to 450°K (350°F). This loss may be attributed to the postulated *in situ* aromatization which is theoretically 4% w/w for the BFBI/BMPM couple.

Based on the result of the precure study summarized in Table IX, a precure reaction employing 422°K (300°F) for eight hours was selected as the cycle for use on the PDA ingredients prior to conducting cure and postcure studies.

TABLE IX

SUMMARY OF PRECURED RESIN PROPERTIES

Resin System	Precure Conditions		Properties of Resin After Precure			
	Precure Temperature (°K/°F)	Precure Duration (Hours)	Resin Melt Point (°K/°F)	On Direct Heating at 505°K	Resin Solubility in DMF (% w/w)	Resin Loss (% w/w)
Pyrolytic Monomer[a]	394/250	4	b	c	d	12
		8	b	c	d	16
		24	b	c	d	e
	422/300	4	b	c	d	e
		8	b	c	d	9
		24	b	c	d	17
	450/350	2	b	c	d	e
		4	b	c	d	e
		8	b	c	d	e
	477/400	1	b	c	d	18
		2	b	c	d	e
		4	b	c	d	18
Poly-(Diels-Alder)[f]	394/250	4	428/310	Complete Melt	100	<1.0
		8	428/310	"	100	<1.0
		24	428/310	"	95	<1.0
	422/300	4	453/356	Complete Melt	95	1.0
		8	453/356	"	90	1.0
		24	458/365	"	90	1.1
	450/350	2	458/365	Complete Melt	<10%	1.5
		4	463/374	"	<10%	1.5
		8	468/383	"	<10%	1.4
	477/400	1	b	Softening Only	d	<1.0
		2	b	"	d	<1.0
		4	b	"	d	<1.0

a. Employing NE/MDA/BTDE (1500 FMW) ingredient combination

b. No melting point observed up to 505°K (450°F) on a Fisher-Johns melting point apparatus using a 2°K/min heat-up rate

c. Only softening observed for samples placed on a melting block preheated to 505°K (450°F)

d. Less than 5% w/w solubility of 1 g sample after heating in DMF (4 g) for one hour at 398°K (260°F)

e. Sample could not be accurately weighed due to loss from foaming

f. Employing stoichiometric mixture of BMPM/BFBI ingredients

3.3.2 Cure and Postcure Studies on Neat Resins

Because 505°K and 1.4 MN/m^2 conditions were shown to provide cure for each resin approach, these conditions were selected as fixed parameters and studies were conducted to investigate the effect of cure time on the reaction. The unstaged ingredients from the PMR approach and PDA ingredients staged for eight hours at 422°K (300°F) were cured for one, two and four hours at 505°K (450°F) and 1.4 MN/m^2 (200 psi) in sealed tubes. Each of the six cured resin samples was then subjected to postcure in nitrogen employing a four-hour linear heat-up rate from 477°K (400°F) to 589°K (600°F), followed by isothermal cycle at 589°K for one, four and eight hours. The results of this experimentation are summarized in Table X.

In order to simplify designation for each of the twenty-four samples shown in Table X, the following code is used:

- PM refers to the pyrolytic monomer approach employing 1500 FMW NE/MDA/BTDE and PDA refers to the poly(Diels-Alder) approach employing BFBI and BMPM.
- The hyphenated number immediately following the letter refers to the hours of sample cure at 505°K (450°F) and 1.4 MN/m^2 (200 psi).
- The last number refers to the hours the particular cured sample was postcured at 589°K (600°F).

In this manner, a sample consisting of 1500 FMW NE/MDA/BTDE which was cured for one hour at 505°K becomes PM-1; this cured sample upon postcure for one hour at 589°K becomes PM-1-1. A sample of BFBI and BMPM cured and postcured for the identical period thus is designated PDA-1-1. This type of nomenclature is used throughout the remainder of this section.

Table X summarizes weight loss observed for all specimens during cure and postcure. For the PMR approach, all samples have a total weight loss (i.e., cure plus postcure) of ∿18% to 22% from the monomeric starting material. The theoretical weight loss of methanol and water to give fully imidized 1500 FMW NE/MDA/BTDE prepolymer is 17% w/w. The total weight percent of cyclopentadiene in the resulting imidized prepolymer structure is 8.8% w/w. Assuming that the weight loss observed during cure (samples PM-1, PM-2 and PM-4) is only methanol and water, all samples lost cyclopentadiene during the postcure cycle. This cyclopentadiene loss ranged

TABLE X

SUMMARY OF CURE AND POSTCURE STUDIES[a]

Cure Duration (Hrs)	Cured Resin Sample[b]	Weight Loss During Cure (% w/w)	Temperature of First Significant TGA Weight Loss of Cured Resin[c] (°K/°F)	Postcure Duration (Hrs)	Postcured Resin Sample[b]	Weight Resin Loss During Postcure (% w/w)	Temperature of First Significant TGA Weight Loss of Resin[c] (°K/°F)
1	PM-1	8.1	635/684	1	PM-1-1	10.2	623/662
				4	PM-1-4	11.2	648/707
				8	PM-1-8	11.1	635/684
	PDA-1	0.2	623/662	1	PDA-1-1	0.9	585/594
				4	PDA-1-4	1.0	623/662
				8	PDA-1-8	1.3	610/639
2	PM-2	14.4	635/684	1	PM-2-1	6.7	635/684
				4	PM-2-4	7.4	648/707
				8	PM-2-8	7.5	648/707
	PDA-2	0.6	623/662	1	PDA-2-1	1.1	623/662
				4	PDA-2-4	1.3	598/617
				8	PDA-2-8	1.2	623/662
4	PM-4	14.6	623/662	1	PM-4-1	5.6	623/662
				4	PM-4-4	6.4	635/684
				8	PM-4-8	6.7	623/662
	PDA-4	0.6	623/662	1	PDA-4-1	0.7	598/617
				4	PDA-4-4	1.1	610/639
				8	PDA-4-8	1.1	610/639

a. All samples were cured at 505°K (450°F) and 1.4 MN/m^2 for indicated duration; all samples were postcured under nitrogen at 589°K for the indicated duration.

b. See context for code

c. TGA conditions employed 3°K/min scan rate and 100 ml/min air flow.

from 15% w/w for sample PM-1-1 to 56% w/w for sample PM-2-8.

A similar phenomenon was observed in Task III studies during the postcure of composites and is discussed in Section IV. The presence of cyclopentadiene in the postcure gaseous effluent was indeed confirmed by mass spectroscopy (MS). The loss of cyclopentadiene, however, did not compromise high initial TOS for the polymer sample produced as discussed later in this section.

A total resin weight loss of up to 1.7% was measured for the PDA system (samples PDA-4-4 and PDA-4-8) (see Table X). When this 1.7% is combined with the 1.0% w/w loss measured during the 8 hour prestaging at 422°K (300°F), as given in Table IX, to give 2.7% w/w total, *in situ* aromatization appears to have occurred to a level of 68% (4.0% w/w resin loss is theoretical), (Prior results discussed in Section 3.2, have confirmed that water is evolved during 589°K (600°F) postcure of the PDA system). Finally, it should be pointed out that this water loss did not impair Task III fabrication of HMS graphite reinforced composites possessing high mechanical properties.

The resin samples obtained from both approaches were found to exhibit excellent TOS's as determined by TGA (Table X). These results indicated that the processing conditions selected, namely a cure duration of two hours at 505°K (450°F) followed by postcure at 589°K (600°F) yield resins of high thermo-oxidative stability in air.

The results of the process studies described above were used as a guide in Task III studies described in the following section. Additional resin work was conducted in Task IV and these studies are discussed in Section V.

IV. TASK III - PROCESS DEVELOPMENT AND EVALUATION

The objective of this task was to develop autoclave molding processes for the poly(Diels-Alder) (PDA) and the polymerization of monomeric reactants (PMR) types of polyimide resins. It was demonstrated during this task that there was reasonable indication that both resins could be processed within the goal fabrication parameters of the program [i.e., $\leq$505°K (450°F) cure temperature and $\leq$1.4 MN/m^2 (200 psi) cure pressure]. Processing procedures were developed for both resin systems, that provided good fiber collimation and wetting while preparing prepreg tapes utilizing the Hercules HMS high modulus graphite fiber tows and either BFBI/BMPM or NE/MDA/BTDE (1500 FMW) resin varnish (see Section 3.3). The concept of starting with prepreg tape possessing sufficient volatile matter content to provide good handling characteristics and then varying the rein flow by the curing process adopted. While processing BFBI/BMPM prepregs, the following three separate cure stages were identified:

- The "A" stage (i.e., volatile removal)
- The "B" stage (i.e., molecular weight "buildup") and
- The "C" stage (i.e., final curing)

4.1 PRELIMINARY PROCESSABILITY EVALUATIONS OF PDA RESINS

In order to determine the temperature at which changes occurred in the candidate PDA resins, studies were commenced using the AUDREY dielectrometer. During these studies, changes in dissipation factor of stacked prepreg as an effect of temperature cycling were recorded. Changes in dissipation factor of these materials during thermal cycling indicated phase changes (i.e., polymer melt and flow) and/or chemical reaction (i.e., chain extension and/or crosslinking). Information from these studies was used while designing the experimental screening test matrices discussed in Section 4.2 of this report.

4.1.1 Audrey Dielectrometer Screening Procedure

An Audrey II dielectrometer and a Moseley 7030 x-y recorder were used to plot changes in dissipation factor vs temperature. Prepreg stacks instrumented with thermocouples and electrodes were placed in an electrically heated hydraulic press which then was heated to a predefined temperature and afterwards cooled back down to room temperature. This cycle was repeated until the curve produced on the cooling cycle was the same as obtained on the heating cycle. When these identical curves were obtained, the polymer was assumed to be fully cured because no measurable changes in dissipation factor were occurring.

4.1.2 Preliminary Process Screening

Prepreg was prepared from Style 181 E-glass fabric, A1100 finish and the BFBI/BMPM resin varnish (30% w/w solids in DMF) to be evaluated. After drying, the prepreg was cut to 5.1-cm by 7.6-cm 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, 0.0016-cm 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 4). Six plies of dry 181 glass fabric were placed on top of the assembly and the press was closed to the desired pressure ($1.4\ MN/m^2$). The Audrey II and Moseley 7030 x-y recorder were connected to the assembly in accordance with the diagram shown in Figure 5.

Screening studies were performed with the Audrey II dielectrometer on the BFBI/BMPM monomer system. The results from these scans showed that the major changes in the polymer's dielectric properties occurred at approximately 466°K (370°F) with the second occurring at 544°K (520°F). This information then was used as a baseline for the molding cycle and postcure cycle process screening studies.

4.2 PROCESS DEVELOPMENT FOR PDA/HMS PREPREGS

Using the AUDREY dielectrometer scans as a guide, processing parameters were investigated in order to define a fabrication procedure for composites containing PDA resin and Hercules HMS graphite fibers.

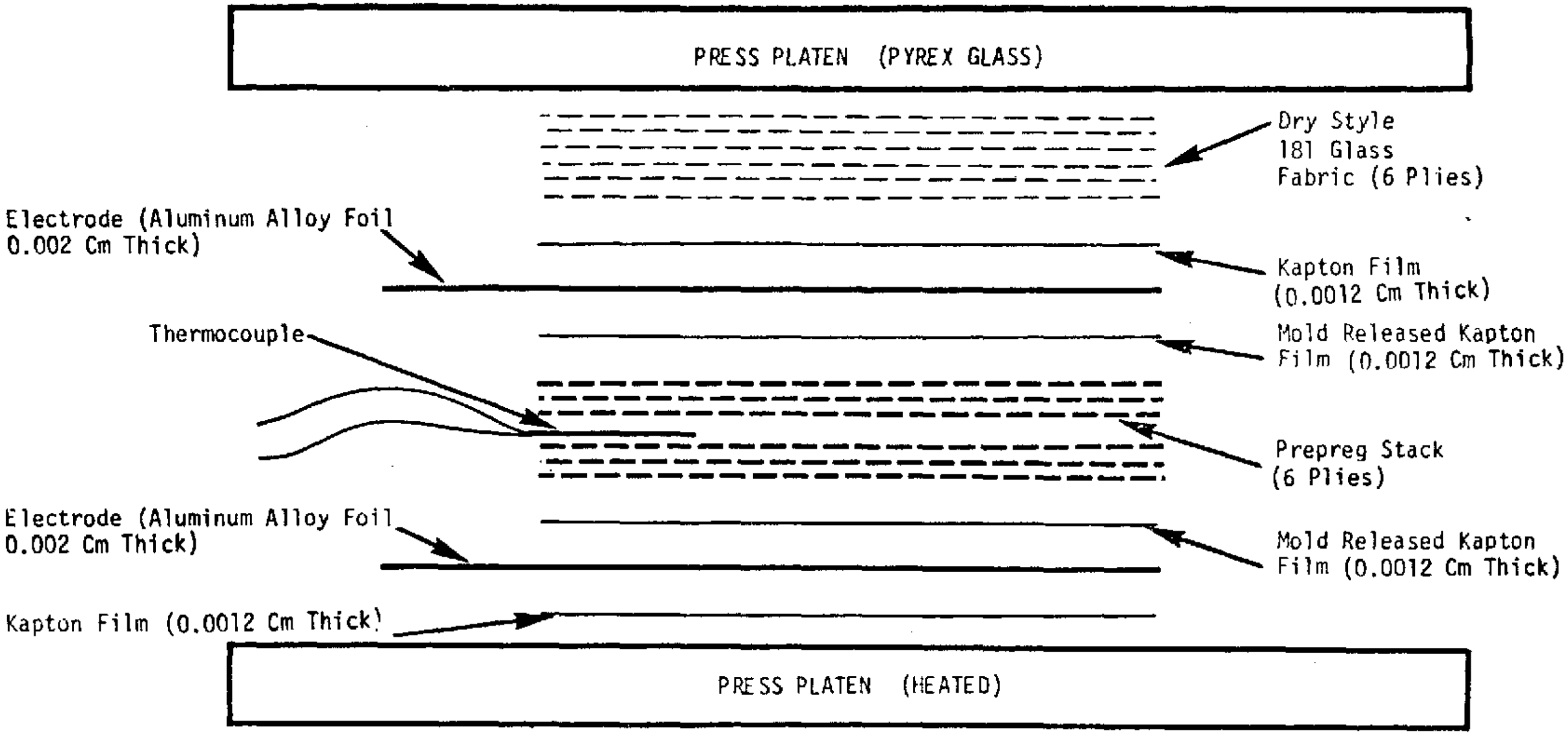


Figure 4. Schematic of Dielectrometer Screening Assembly

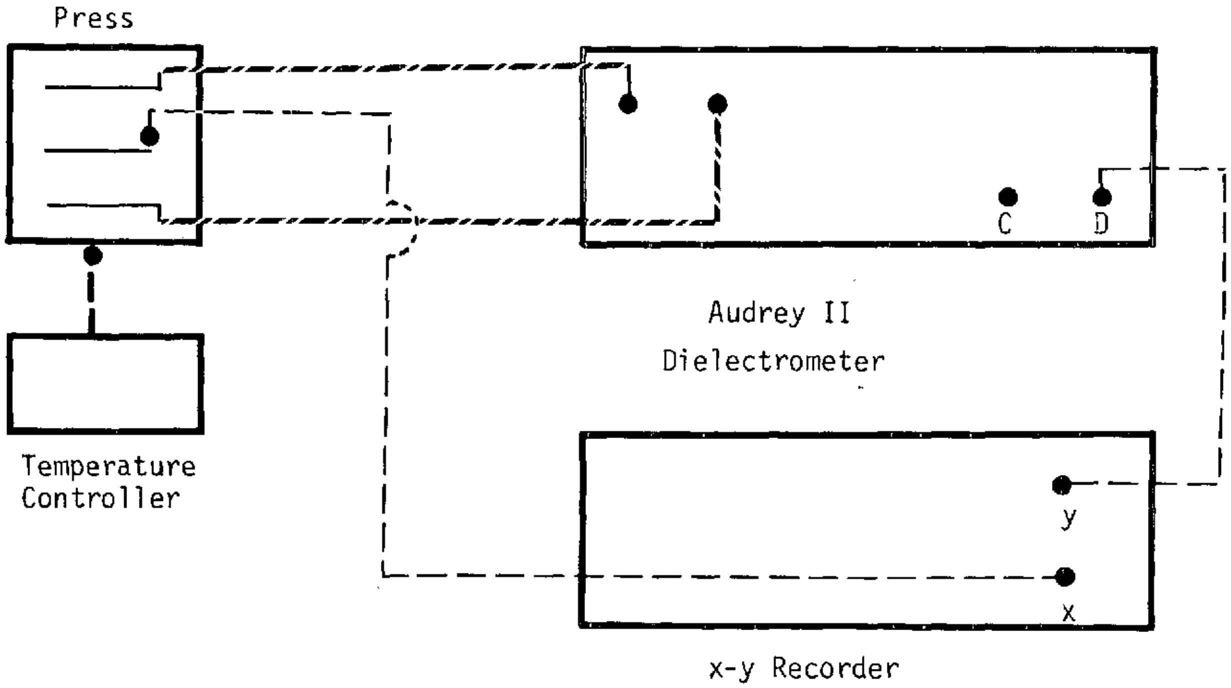


Figure 5. Wiring Diagram For Dielectrometer Experiments

4.2.1 Prepreg Preparation and Characterization

Hercules HMS high modulus graphite fiber tows were impregnated with BFBI/BMPM resin varnish (30% w/w resins solid) and collimated by drum winding at 35-36 tows/meter. Resin content level of the prepreg was maintained by controlling the resin solids of the varnish in the resin bath. Winding rate was approximately 20 cm/sec on a 46.2-cm diameter drum. The graphite tape was air dried on the drum until the tape possessed the desired handling properties.

Characterization of the prepregs consisted of volatile matter content and resins solids determinations. The volatile matter contents were determined by the weight loss of a prepreg sample in an air circulating oven at 560°K (550°F) for 30 minutes. Resin solids contents were determined by acid digestion of the retained, cured, volatiles content specimen.

4.2.2 Process Variation Studies

The graphite tape was cut into 5.0-cm x 18-cm (fiber direction) pieces and stacked 7-plies thick. The stacked prepreg then was vacuum bagged as follows:

> Zinc chromate sealant tape was placed around the periphery of an aluminum caul plate. A mold released piece of Kapton film 24-cm x 38-cm was placed on the caul plate on top of which was placed the stacked prepreg. On top of the prepreg stack was placed another piece of mold released Kapton film the same size as the prepreg stack. Around the prepreg were placed strips of style 181 glass fabric, the prepreg and the glass were not allowed to be in contact. A thermocouple was inserted into the prepreg stack between the fourth and fifth plies. A stainless steel hydraulic tube was placed in between the style 181 glass fabric, the layup was covered with Kapton film and a vacuum was drawn.

The vacuum bag layup was inserted into a hydraulic press and then processed per the applicable processing cycle. Due to the large number of possible process variables to be studied, two fractional factorial experiments were chosen to obtain preliminary data that would indicate the most important factors to be evaluated later in the program. The conditions selected for the first fractional factorial screening study were based on data obtained during the Audrey II screening of the resin varnish.

The specific matrix design was selected in order to explore the combinations of two "A" stage temperatures; two "A" stage times, two "B" stage temperatures and two "B" stage times. Details of this matrix are provided in Figure 6. The data derived from this design were the main effects of the variables and at most, the major first order interactions (i.e., AB, CD). All other information was considered minor for the purpose of this preliminary experiment. The "C" stage conditions in this study were held constant and were 0.70 MN/m^2 (100 psi), 505°K (450°F) and 2 hours 560°K (550°F). Composites were manufactured using the simulated autoclave technique and the above matrix conditions. The physical and mechanical properties were determined on the composites (see Table XI) and a least square statistical analysis of the flexural strength and shear strength data was performed (see Tables XII and XIII) according to the method

FIGURE 6
Processing Studies Matrix

Expt	Factors/Condition[a]			
	A	B	C	D
1	-	-	-	+
2	+	-	-	-
3	-	+	-	-
4	+	+	-	+
5	-	-	+	-
6	+	-	+	+
7	-	+	+	+
8	+	+	+	-

a) Code for factors/conditions matrix

Factor		+	-
A	"A" stage temperature	380°K (225°F)	350°K (170°F)
B	"A" stage time	120 min	60 min
C	"B" stage temperature	440°K (332°F)	420°K (297°F)
D	"B" stage time	60 min	30 min

described by Davies (Reference 9). It was observed from the data in Table XII, that Factors B, D and interactions AB and CD appeared to be significant. In addition, based upon the R.T. flexural strength values (see Table XIII), Factor C appeared to be significant along with the factors mentioned in Figure 6. Also from Table XIII, Factor AC, BD also could be considered to be significant. However, based on past experience and the information desired from this matrix design, the elimination of this interaction (AC, BD) was accomplished. Therefore, based on the statistical analysis (Tables XII and XIII) it was determined that for the purpose of the second fractional factorial design, the best conditions obtained within the limits of the test matrix "A" stage conditions of 380°K (225°F) for 120 minutes and the "B" stage conditions 440°K (332°F) and for 30 minutes.

The second fractional factorial screening was conducted in order to obtain preliminary information concerning the "C" stage curing conditions. The parameters evaluated during this study were the "C" stage cure temperature, cure time and cure pressure along with postcure temperature and time. Two levels of each condition were evaluated as shown in Figure 7 and were based on data obtained from Audrey II scans. The information desired from this matrix design were the main effects of the variables and the major first order interactions. The "A" stage condition for the purpose of this experiment remained the same as selected previously (i.e., 120 minutes at 380°K, 30 minutes at 440°K with the pressure being applied at the end of the 440°K dwell cycle). The physical and mechanical properties then were determined on composites made using the simulated autoclave arrangement and with processing conditions defined in the above matrix (see Table XIV). In addition to the room temperature property determinations, flexural strengths at 589°K (600°F) also were determined and are presented in the same table. A statistical analysis similar to the one above was performed using room temperature flexural strength, room temperature shear strength and 589°K (600°F) flexural strength values (see Tables XV, XVI and XVII). Analysis of room temperature flexural strength data in Table XV indicated

TABLE XI

SUMMARY DATA - A AND B STAGE CURE STUDY

A-Stage Cycle		B-Stage Cycle		Tape Properties		Laminate Physical Properties				Laminate Mechanical	
Hrs.	°K	Hrs.	°K	Volatile Matter Content % v/v(1)	Resin Content, % w/w	Density, g/cc (2)	Resin Content, % w/w	Void Volume, % v/v (5)	Fiber Volume, % v/v (6)	Flexural Strength, MN/m^2 (3)	Short Beam Strength MN/m^2 (4)
1	350	1	420	--	24.6	1.590	26.5	8.0	59.6	647	34.7
1	380	0.5	420	--	34.3	1.566	22.4	11.0	62.0	558	29.1
2	350	0.5	420	4.8	33.4	1.625	23.8	7.1	63.2	611	43.5
2	380	1	420	16.0	33.4	1.516	23.2	13.5	59.4	794	44.4
1	350	0.5	440	9.8	34.0	1.635	21.7	7.4	65.3	666	45.0
1	380	1	440	9.5	34.7	1.493	27.6	13.2	55.4	564	25.9
2	350	1	440	12.8	38.7	1.506	29.8	11.5	53.9	1004	35.5
2	380	0.5	440	--	33.4	1.542	25.9	10.9	58.2	742	51.2

1) Volatiles matter content determined by weight loss of graphite tape when exposed 30 minutes at 560°K (550°F).

2) Density was determined by physical measuring of the specimens and calculated $D = \frac{\text{Weight}}{\text{Volume}}$

3) The testing span was 32 times the specimen depth.

4) Specimen length was 6 times the specimen depth. The testing span was 4 times the specimen depth.

5) Calculated from measured density and resin content values.

6) Calculated from measured resin content value.

TABLE XII
STATISTICAL ANALYSIS OF R.T. SHORT BEAM STRENGTH

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Sum of Square
A	- 8.1	- 2.0	1	8.2
B	31.8	8.0	1	126.4
C	5.9	1.5	1	4.4
D	-28.3	- 7.1	1	100.1
AB,CD	41.3	10.3	1	213.2
AC,BD	1.3	0.3	1	0.2
AD,CD	8.3	2.1	1	0.6

TABLE XIII
STATISTICAL ANALYSIS OF R.T. FLEXURAL STRENGTH

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Sum of Square $(\text{Col } 2)^2/8$
A	-269.2	67.3	1	9,058
B	716.4	179.1	1	64,153
C	365.4	91.4	1	33,379
D	433.0	108.3	1	23,436
AB,CD	112.0	28.0	1	1,568
AC,BD	-458.1	-114.5	1	26,232
AD,CD	-315.0	- 78.6	1	12,403

FIGURE 7

Processing Studies Matrix

Expt	Factors/Condition[a]				
	A	B	C	D	E
1	-	-	-	-	-
2	+	-	-	+	-
3	-	+	-	+	+
4	+	+	-	-	+
5	-	-	+	+	+
6	+	-	+	-	+
7	-	+	+	-	-
8	+	+	+	+	-

a) Code for factors/conditions matrix

Factor		+	-
A	"C" stage temperature	505°K (450°F)	473°K (390°F)
B	"C" stage time	4 hours	2 hours
C	"C" stage pressure	0.70 MN/m^2 (100 psi)	0.35 MN/m^2 (50 psi)
D	postcure temperature	589°K (600°F)	560°K (550°F)
E	postcure time	16 hours	4 hours

Factors A, -DE and AB could be significant. Further analysis of interaction AB indicated that Factor A conditions should be 472°K and Factor B should be 2 hours. This latter fact (i.e., Factor B should be at 2 hours) also was demonstrated in the analysis of Table XVII room temperature shear data. Analysis of the 589°K flexural strength (see Table XVI) supported the view that Factor A, -DE and B, -CE were significant. In addition, the results in Table XVI indicated that better elevated temperature retention could be obtained with the higher postcure temperature. It could be summarized that the information obtained from the "C" stage cure matrix indicated that the BFBI/BMPM system could be processed at 472°K (390°F) cure temperature, 2 hours cure time, 0.35 MN/m^2 (50 psi) molding pressure and either of the postcure conditions and obtain reasonable room temperature composite properties. However, it should be noted that the preliminary results

TABLE XIV
SUMMARY DATA "C" CURE STUDY

C-Stage Cycle			Postcure Cycle		Tape Properties			Laminate Physical Properties				Laminate Mechanical			
Hrs.	°K	MN/m²	Hrs.	°K	Volatile Matter Content % w/w	Resin Content, % w/w	Density, g/cc (5)	Resin Content, % w/w	Void Volume, % v/v (6)	Fiber Volume, % v/v (7)	Flow Volume, % w/w (1)	Flexural Strength, MN/m² (2)	Short Beam Strength, MN/m² (3)	Test Temperature °K	% Retention (4)
2	473	0.35	4	560	8.6	38.5	1.636	28.5	4.5	59.7	12.4	855 697	51.3	295 589	81.6
2	505	0.35	4	589	8.6	38.5	1.660	27.6	3.4	61.3	12.4	654 558	36.7	295 589	85.4
4	473	0.35	16	589	20.0	36.0	1.663	25.4	4.2	63.5	20.4	671 628	32.1	295	93.5
4	505	0.35	16	560	19.5	33	1.675	28.2	2.3	61.4	5.5	756 472	31.8	295 589	62.4
2	473	0.70	16	589	8.6	38.5	1.661	26.8	3.7	62.0	13.0	816 766	45.3	295 589	94.0
2	505	0.70	16	560	19.0	29.0	1.687	24.3	5.0	65.2	8.6	503 402	39.5	295 589	80.1
4	473	0.70	4	560	19.0	29.0	1.675	23.0	4.5	65.8	10.7	715 554	35.9	295	77.6
4	505	0.70	4	589	19.5	33.0	1.680	22.8	4.4	66.2	15.4	634 461	30.6	295 589	72.7

1) % Flow $\frac{\text{Dry Weight of Prepreg} - \text{Cured Composite Weight}}{\text{Dry Weight of Prepreg}} \times 100$

2) The test span was determined by multiplying the specimen thickness by 32.

3) The specimen length was 6 times specimen thickness and the test span was 4 times specimen thickness.

4) % Retention - $\frac{\text{Flexural Stress at 589°K}}{\text{Flexural Stress at 295°K}} \times 100$

5) Density was determined with the following formula - $\frac{\text{Specimen Weight in air}}{\text{Specimen Weight in Air} - \text{Specimen Weight in Water}}$

6) Calculated from measured density and resin control values.

7) Calculated from measured resin content value.

indicated that for the best elevated temperature retention the higher postcure temperature and time is desirable.

TABLE XV
STATISTICAL ANALYSIS OF R.T. FLEXURAL STRENGTH

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Mean Square (col 2)^2/8
A, -DE	-1018.9	-254.7	1	129,770
B, -CE	- 51.0	- 12.8	1	325
C, -BE	- 267.8	- 67.0	1	8,965
D, -AE	- 54.2	- 13.6	1	367
E, -AD, -BC	- 111.2	- 27.8	1	1,546
AB, CD	517.2	129.3	1	33,436
AC, BD	- 277.2	69.3	1	9,604

TABLE XVI
STATISTICAL ANALYSIS OF 589°K FLEXURAL STRENGTH

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Mean Square (Col 2)^2/8
A, -DE	-752.5	-188.1	1	70,782
B, -CE	-307.3	- 76.8	1	11,804
C, -BE	-172.1	- 43.0	1	3,702
D, -AE	288.1	72.0	1	10,375
E, -AD, -BC	67.7	16.9	1	572
AB, CD	253.9	63.5	1	8,058
AC, BD	161.9	- 40.5	1	3,276

TABLE XVII

STATISTICAL ANALYSIS OF R.T. SHEAR STRENGTH PROPERTIES

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Mean Square $(Col\ 2)^2/8$
A, -DE	-26.0	-6.5	1	84.5
B, -CE	-68.4	-7.1	1	584.8
C, -BE	- 0.9	-0.2	1	0.1
D, -AE	-14.7	-3.7	1	27.0
E, -AD, -BC	- 5.8	-1.5	1	4.2
AB, CD	14.8	3.7	1	27.4
AC, BD	3.8	1.0	1	23.8

4.2.3 Preliminary Isothermal Aging of a BFBI/BMPM Composite

In order to obtain an early assessment of the PDA-type resins potential, an isothermal aging study was conducted on a BFBI/BMPM-HMS reinforced composite. This laminate sample was prepared by the autoclave molding process described previously in Section 4.2.2 and aged at 561°K (550°F) in a circulating air oven. Weight retention results obtained on the composite are shown in Figure 8 and pertinent laminate properties obtained are shown in Table XVIII. These results show promise for the PDA approach to prepare acceptable laminates by autoclave molding processes.

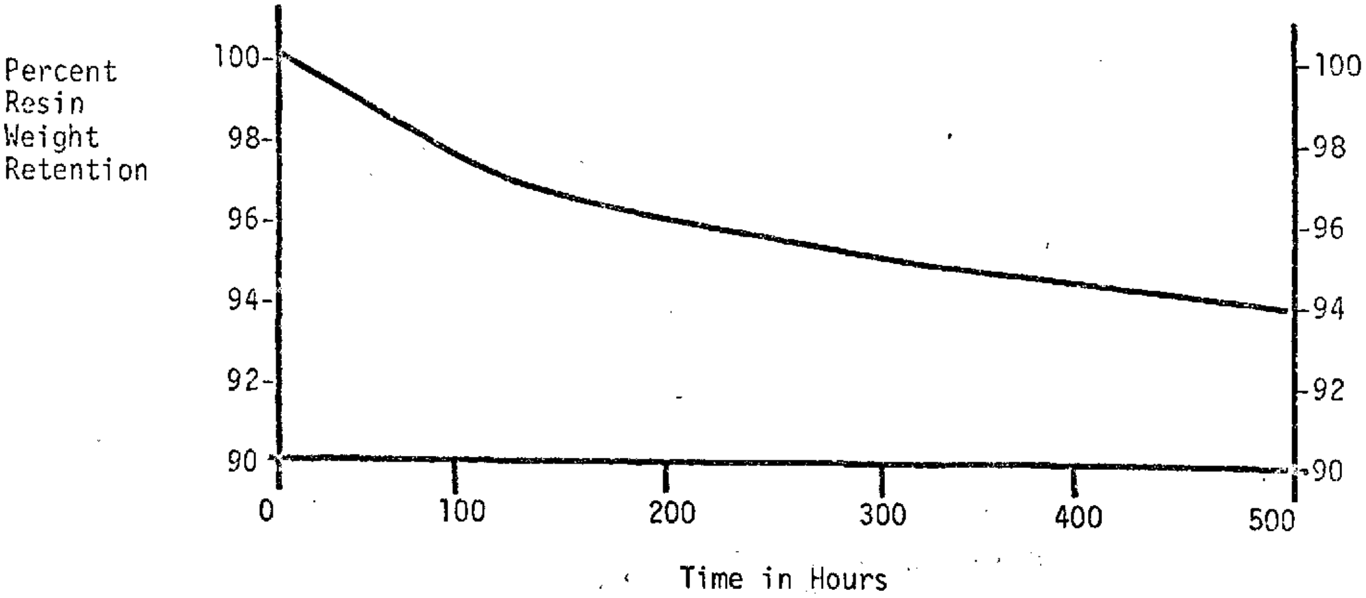


Figure 8. Preliminary BFBI/BMPM Composite Aging Results

TABLE XVIII

PRELIMINARY BFBI/BMPM COMPOSITE PROPERTY RETENTION ON AGING AT 561°K IN AIR[a,b]

Property[c]	Initial Values		After 500 Hour Exposure		Retention (%)
	at R.T.	at 589°K	at R.T.	at 589°K	
Flexural Strength	86.5 MN/m^2 (123.5 Ksi)	88.9 MN/m^2 (127.5 Ksi)	-	97.1 MN/m^2 (138.7 Ksi)	100+
Interlaminar Shear Strength	36.7 MN/m^2 (5.3 Ksi)	-	30.8 MN/m^2 (4.3 Ksi)	-	80

a. Aged in air circulating oven at a flow rate of 76.1 liters/min employing flex coupon dimensions of 0.24 cm x 1.27 cm x 10.2 cm and shear specimen dimensions of 0.24 cm x .61 cm x 1.44 cm.
b. Properties given are average of duplicate determinations.
c. Other properties of the composite: Resin content = 25% w/w; Specific gravity = 1.726; Fiber volume = 65.1%; Void content = -1.4%.

Another promising result was evidence for the composite used in this study to be void free. A cross-section of the composite at 800X magnification is shown in Figure 9. This photomicrograph supports the theory that the postulated *in situ* aromatization can be effected in an autoclave to give void free specimens.

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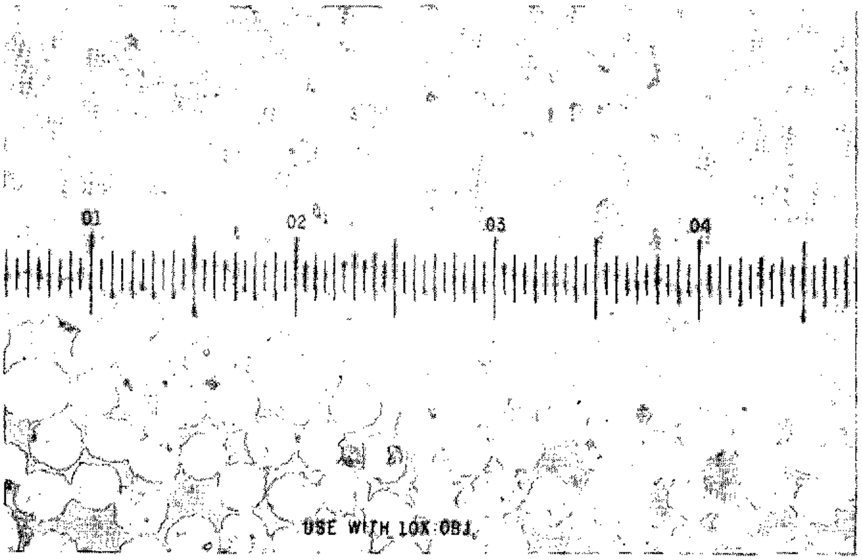


Figure 9. Photomicrograph of BFBI/BMPM-HMS Composite (800X)

4.3 PROCESS DEVELOPMENT FOR PMR/HMS PREPREGS

Similar processing studies were performed with polyimide resins using the PMR approach as were conducted with resins from the PDA approach. Procedures for preparing handleable prepreg tapes from PMR resin and Hercules HMS graphite fiber were investigated. Subsequently, autoclave molding cycles for the PMR/HMS prepreg tapes were investigated and preliminary mechanical property information was obtained.

4.3.1 Preliminary PMR Resin Processing Studies

Graphite tape prepregs were prepared from the NE/MDA/BTDE resin using Hercules HMS graphite fiber tow (see Section 3.3). These tapes then were molded using a simulated autoclave molding process and the layup procedure described in 4.2.2. The first series of laminates were fabricated to determine whether the resin varnish could be processed within the parameters of this program [i.e., <505°K (450°F) cure temperature and <1.4 MN/m^2 (200 psi) cure pressure]. The only parameter evaluated during this study was cure time, i.e., 4, 6 and 16 hours; all other parameters were held constant, i.e., 30 minutes dwell at 350°K (170°F), 45 minutes dwell at 394°K (250°F), apply 0.7 MN/m^2 (100 psi) pressure and then raise the temperature to 505°K (450°F). Postcure was 4 hours at 589°K (600°F). Physical and mechanical properties were determined on the resultant composites (see Table XIX) and the flexural strength of 1100 MN/m^2 indicated that the methyl ester approach was indeed viable.

4.3.2 Detailed PMR Resin Processing Studies

A detailed process screening study similar to the one used previously for the PDA prepregs then was initiated. During the early stages of this study a serious problem was identified in that fiber washout occurred which was caused by the loss of resin during the curing cycle. The most probable cause of this problem was the very low viscosity of the combination of monomer/residual solvent during the "A" and/or "B" stages. Evaluation of the prepreg tape data used to fabricate the previous sucessful laminates, showed that most of the acceptable laminates were made from tapes with volatile matter content <10% w/w whereas the panels having the "fiber-washing" problem came from tape with volatile matter content >13% w/w.

TABLE XIX

PROPERTIES OF AUTOCLAVE MOLDED HMS - NE/MDA/BTDE COMPOSITES

Prepreg Properties			Laminate Properties			
Cure Time Hours @ 505°K	Volatile Content[1] % w/w	Resin Content % w/w	Flexural Strength MN/m² (2)	Short Beam Shear Strength MN/m² (3)	Resin Content % w/w	Density g/cc (4)
4	9.0	37.2	1168	38.0	23.9	1.54
6	9.0	37.2	1115	44.4	26.9	1.59
16	13.6	36.5	984	33.7	26.3	1.50

1. Volatile matter content determined 30 minutes at 505°K (550°F)
2. Testing span was 32 times specimen depth
3. Testing span was 4 times speciment depth. Specimen length was 6 times specimen depth
4. Density was determined using ASTM D792-66 and the formula:

$$\frac{\text{weight specimen in air}}{\text{weight specimen in air - weight specimen in } H_2O}$$

When the volatile matter content of the NE/MDA/BTDE prepreg tape was below 13% w/w it was stiff and boardy and therefore, not in keeping with the "handleable tape" criteria. Different approaches then were investigated in an attempt to eliminate the problem. These included release of vacuum during "B" staging, change of solvents (i.e., from DMF to methanol) and addition of a thixotropic agent. Composites then were fabricated using the simulated autoclave technique and the physical and mechanical properties were determined (see Table XX). This study indicated that use of a thixotropic agent provided promising results and probably was the most practical approach. The addition of 3% Cab-O-Sil (based on resin solids) drastically changed the tape and processing characteristics (i.e., from 14 to 2 percent resin flow). Therefore this method of limiting flow was evaluated further during Task IV studies (see Section 5.2.2).

TABLE XX
NE/MDA/BTDE FLOW STUDIES

Prepreg Properties			Laminate Properties				
Solvent Used in Resin Varnish	Volatile Matter Content % w/w (1)	Resin Content % w/w	Resin Flow % w/w (2)	Resin Content % w/w	Specific Gravity (3)	Flexural Strength @ R.T. (4) MN/m^2	Shear Strength @ R.T. MN/m^2
DMF	13.0	37.7	14.5	(6)	(6)	(6)	(6)
DMF	13.6	37.5	13.6	(6)	(6)	(6)	(6)
DMF (7)	10.8	37.2	8.0	32.5	1.47	898	43.6
DMF (7)	9.0	38.0	3.5	31.5	1.62	1023	39.9
MeOH (7)	9.0	40.0	14.0	(6)	(6)	(6)	(6)
DMF (8)	17.0	50.0	1.8	(6)	(6)	(6)	(6)

Cure cycle - Vacuum. Raise temperature to 350°K for 1 hour, 395°K 1 hour, 0.7 MN/m^2 (100 psi) positive pressure and raise to 505°K (450°F) 4 hours. Cool under vacuum. Postcure 4 hours @ 589°K (600°F).

(1) Volatile matter determine on weight loss after 30 minutes 560°K (550°F).

(2) Flow determine using $\frac{\text{Weight loss of composite during cure}}{\text{Dry weight of composite before cure}} \times 100$

(3) Specific Gravity determined using ASTM D792-66 and the formula: $\frac{\text{weight specimen in air}}{\text{weight specimen in air - weight specimen in } H_2O}$

(4) Testing span was 32 times specimens depth.

(5) Testing span was 4 times specimens depth. Specimen length was 6 times specimen depth.

(6) Panel was of poor quality and no tests were conducted.

(7) Panel had vacuum removal during "B" stage (i.e., after 350°K dwell time and restarted when 0.7 MN/m^2 was applied.

(8) Addition of 3% Cab-O-Sil based on resin solids.

It was concluded from this work that the PMR approach was of equal promise to the PDA route as a means to prepare reinforced composites in an autoclave employing mild process conditions. Additional work was performed on both resin approaches as described in the next section.

V. TASK IV - RESIN AND PROCESS MODIFICATION STUDIES

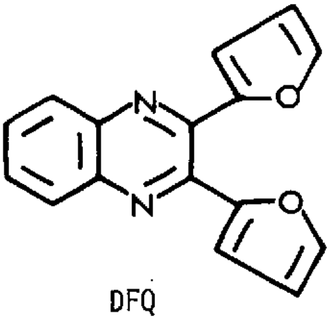
The objective of work conducted in this task was to investigate improvements in the promising resin approaches that were developed in Task II and evaluated in Task III. The modification studies were designed to optimize the thermo-oxidative stability and/or the processability of the resins through evaluations of neat polymer and HMS graphite fiber reinforced composites. The results of this study are discussed in detail in the following sections.

5.1 RESIN MODIFICATION STUDIES

The results obtained in Task II and Task III indicated that two approaches for accomplishing the autoclavable cure objectives of the program had been identified. However, the findings also indicated a need for resin and/or process modification to achieve a higher combination of thermo-oxidative stability (TOS)/processability/mechanical property characteristics. The resin modification studies of this task were concentrated on potential upgrading of the TOS of polyimides prepared by the PDA technology.

5.1.1 New PDA Resin Screening

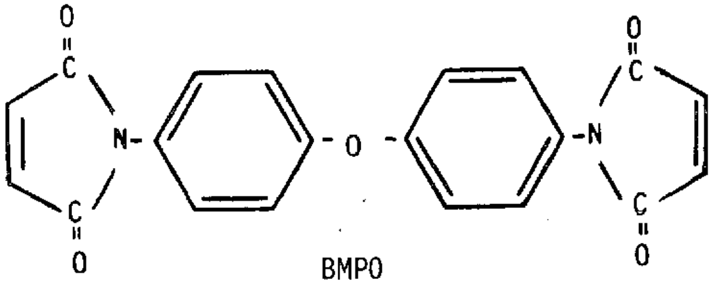
The PDA resin selected for use in Task III employed BFBI and BMPM as a result of Task II work. It was felt that the presence of methylene groups in both the BFBI and BMPM monomer represented a weak link in the resultant polymer system. To eliminate the methylene group, a new bis(furan) monomer, 2,3-di-α-furylquinoxaline (DFQ), was selected as a possible replacement for BFBI. This structure has no oxidatively labile methylene group and also offered the potential stability of a quinoxaline ring system and higher solubility in process solvents than BFBI.



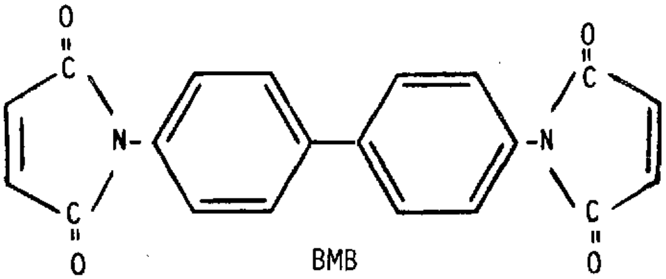
DFQ

The synthesis route used to prepare the difuryl quinoxaline was essentially that of Hartman and Dickey (Reference 10). The reaction of furil (prepared by oxidizing the benzoin condensation product of furfural) with *o*-phenylenediamine in acetic acid gives the quinoxaline in high yield. The experimental details are given in Appendix C.

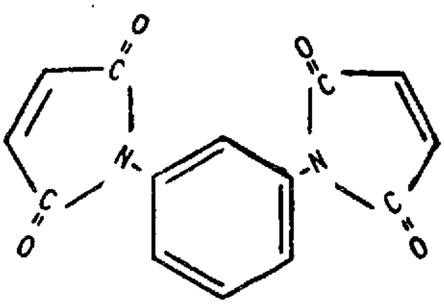
In addition to substituting DFQ for BFBI, the resin modification study was expanded to include three alternative bis(maleimides) to BMPM for the same reason as the DFQ selection (i.e., elimination of the methylene linkage). The three new bis(maleimides) selected were bis(4-maleimidophenyl) oxide (BMPO), bis(4-maleimido) biphenyl (BMB) and 1,3-dimaleimidobenzene (DMB). In addition to providing potential increased TOS, the new bis(maleimides) provide increased stiffness to polymers over that demonstrated by the BFBI/BMPM combination.



BMPO



BMB



DMB

The polymerization conditions demonstrated for the BFBI/BMPM resin, as discussed in Section 3.3, were employed in this study and consisted of cure at 505°K and 1.4 MN/m^2 for 2 or 4 hours and postcure in nitrogen for four hours at 589°K (600°F). The polymer samples obtained were analyzed by TGA for initial TOS. The results of this study are presented in Table XXI.

TABLE XXI

INITIAL TOS OF DFQ DERIVED POLYIMIDES

Maleimide	Cure[a] duration, hr.	Temperature of[b] First Significant TGA Weight Loss of Resin (°K/°F)	Temperature[b] of First Significant TGA Weight Loss of Postcured Resin (°K/°F)
BMPM	2	598/617	623/662
BMPO	4	610/639	623/662
BMB[c]	4	d	610/639
DMB	4	623/662	648/707

a. Pyrolysis conditions
505°K (450°F) and 1.4 MN/m^2 (200 psi)

b. TGA conditions employed 3°K/min scan rate and 100 ml/min air flow

c. No melt flow during pyrolysis

d. Not determined

The polymerization residues obtained under these conditions from DFQ and the various maleimides were consolidated plugs with one exception, the bis(maleimide) of benzidine (BMB). In this case, the sample only partially melted and a sintered solid was obtained.

All of the resin samples showed high TOS after postcure. The DFQ/BMPM sample exhibited the same thermo-oxidative stability as that of the BFBI/BMPM system previously studied. This result substantiates the hypothesis that the weak link in the system is the methylene group in the BMPM, as well as that in BFBI. Substituting bis(maleimidophenyl) oxide (BMPO) for BMPM did not result in a higher TOS, indicating that an oxygen link is about equivalent to $-CH_2-$ in this system. The lower TOS of the BMB (which contains no easily oxidized group), was ascribed to incomplete cure.

The most promising results were obtained on the DFQ/1,3-dimaleimidobenzene (DMB) resin. This bis(maleimide) is similar to BMB in that it contains no easily oxidized groups and should consequently give a polymer system possessing the highest TOS. This was indeed the case, as can be seen in Table XXI, the DFQ/DMB resin was 25°K (45°F) higher in initial TOS than any PDA resin prepared during Task II studies and is equivalent in TOS to the best samples prepared by the PMR approach. In addition, the DFQ/DMB system was equivalent in excellent melt processability to its BFBI/BMPM forerunner. The postulated chemistry of a PDA reaction to form the DFQ/DMB resin is shown in Figure 10.

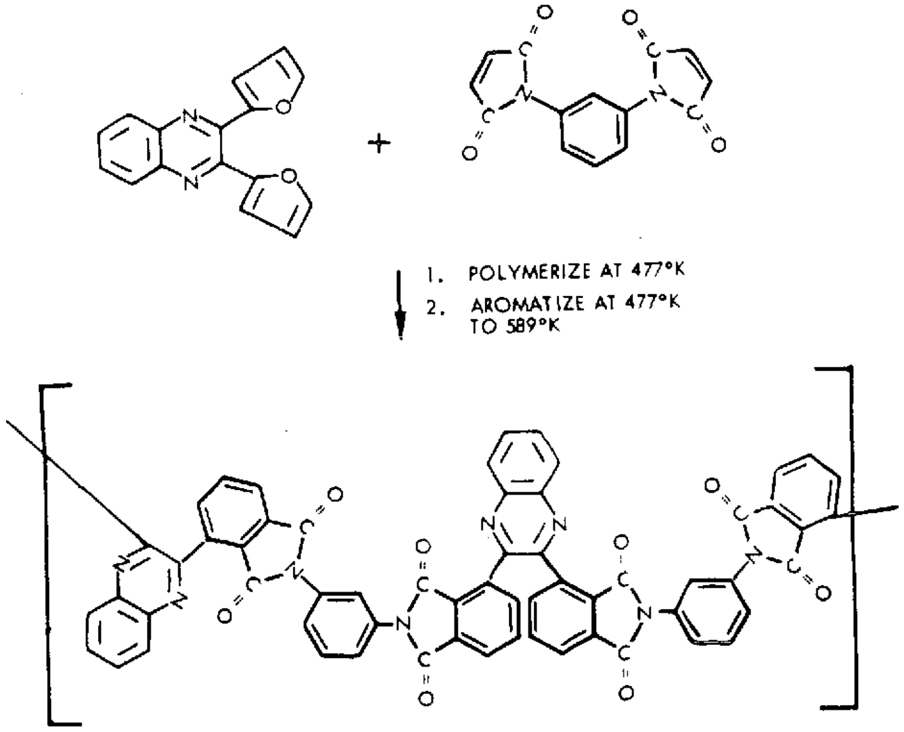


Figure 10. Chemistry of PDA Reaction to Form The DFQ/DMB Resin

Detailed investigations were then performed on the DFQ/DMB modification as described in the following paragraphs.

5.1.2 DFQ/DMB Cure/Postcure Studies

Due to the high initial promise shown by the DFQ/DMB system, additional cure studies were conducted to define conditions that would result in a resin possessing property improvements over the BFBI/BMPM polymer. A brief matrix study on cure and postcure conditions was performed based on the conditions used previously for the BFBI/BMPM couple. In this study, a stoichiometric mixture of DFQ/DMB ingredients was cured for two, four and eight hours at 505°K (450°F) and 1.4 MN/m^2 (200 psi). The polymerization residues obtained under these conditions were subsequently ground to a fine powder and postcured in nitrogen employing a four-hour linear heat-up rate from 477°K (400°F) to 589°K (600°F), followed by an isothermal cycle at 589°K for two, four and eight hours. The results of this experimentation are summarized in Table XXII.

The significant result obtained from this experimentation was that all the postcured samples exhibit essentially the same initial TOS. A small increase in ITOS ($\geq$7°K/13°F) was observed in three samples, all of which were cured and postcured for longer periods of time. Based on these results, the processing conditions selected for the DFQ/DMB mixture were cure of 4 hours at 505°K followed by 8 hours of postcure at 589°K. These conditions were selected as a compromise between resin property build-up and time requirement for cure under autoclave conditions.

5.1.3 Additional DFQ/DMB Resin Studies

Initial attempts to process the unstaged DFQ/DMB mixture as a varnish in DMF indicated that as the solvent was removed the monomers were directly precipitated on the graphite fibers giving a flaky prepreg which was difficult to handle. On further heating in a typical autoclave cycle, the monomers also exhibited too much flow. Screening studies were conducted on solubility in an alternative solvent to DMF, namely N-methylpyrrolidinone (NMP). The DFQ/DMB monomers exhibited higher initial solubility

TABLE XXII
SUMMARY OF CURE AND POSTCURE STUDIES ON DFQ/DMB MIXTURE[a]

Cure Duration, hr.	Temperature of Initial Weight Loss in TGA (°K/°F)[b]	Postcure Duration, hr.[c]	Temperature of Initial Weight Loss in TGA Postcured Resin (°K/°F)
2	486/415 (1st) 623/662 (2nd)	2	623/662
		4	623/662
		8	623/662
4	486/415 (1st) 623/662 (2nd)	2	623/662
		4	623/662
		8	636/685
8	473/392 (1st) 623/662 (2nd)	2	623/662
		4	636/685
		8	636/685

a. Employing stoichiometric mixture of DFQ/DMB ingredients

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

c. Postcure cycle consisted of 4 hour linear heat-up from 477°K (400°F) to 589°K (600°F) followed by isothermal cycle for stated time period at 589°K (600°K) under nitrogen

in NMP than DMF (i.e., 30% to 35% w/w vs 25% to 30% w/w, respectively). The prepreg precipitation problem remained, so an approach was investigated to prestage the monomer mixture and develop a low molecular weight prepolymer which was still soluble in the solvent system. Accordingly, a mixture of the monomers was heated at 450°K (350°F) under nitrogen for different time periods. The resulting samples were checked for solubility in NMP at 30% (w/w) concentration and, if found to be soluble, their inherent viscosity was determined. The results of this study are presented in Table XXIII.

TABLE XXIII
SUMMARY OF DFQ/DMB PRECURED
RESIN PROPERTIES

Precure Duration (Hrs)	Weight Loss[a] (% w/w)	Solubility in NMP at 293°K (% w/w)	Inherent Viscosity (in NMP)
0		>30	0.03
2	2.3	>30	0.04
4	3.6	>30	0.03
8	5.6	>30	0.05
9.5	6.0	>30	0.06
16	10.0	< 5	c

a. Open container in oven

b. Heated at 450°K

c. Not determined due to low solubility

These results indicated that a gradual increase in the inherent viscosity of the mixture can be effected at 450°K (350°F). The sixteen hour sample was a solid at 450°K and was insoluble in NMP indicating that the resin had been advanced too far. The eight hour sample was selected as being most promising because of the increase in molecular weight and, in addition, it offers an added feature in that at least two more hours of heating are required before an intractable resin is obtained. This time margin is very important to avoid the loss of resin (i.e., too rapid cure) in actual processing.

This resin was employed to fabricate HMS reinforced composites as described in Section 5.2. Isothermal aging studies were conducted on the DFQ/DMB resin as well as the PDA and PMR formulations identified as promising in earlier studies (see Section 3.3). The aging studies are described in the following section.

5.1.4 Isothermal Aging Studies on PMR and PDA Candidates

The experimental results obtained previously in this program for a PDA resin system (see Section 4.2.3) or eleswhere for the PMR derived polyimide (Reference 7) indicated that both polymers should meet the 561°K (550°F) minimum long-term isothermal stability in air objective of the program. As was discussed in Section 5.1, the DFQ/DMB combination was designed to offer higher temperature performance than either the BFBI/BMPM system or the 1500 FMW NE/MDA/BTDE resin derived by the PMR approach. However, some unexpected results were obtained when samples of each candidate resin were isothermally aged in air at 561°K (550°F) and 589°K (600°F) for up to 1000 hours in air as neat resin plugs.

The results of the isothermal aging study are summarized in Table XXIV. Two samples each of BFBI/BMPM, DFQ/DMB and 1500 FMW NE/MDA/BTDE, processed under the different temperature or time conditions shown in Table XXIV, were aged at 561°K and 589°K in flowing air (100 ml/min). Resin weight loss was determined at three to five time intervals over an aging period of up to 1000 hours as shown in Table XXIV and graphically represented in Figure 11.

This key study demonstrated several significant factors concerning each resin candidate and the polymerization (i.e., PMR or PDA). General conclusions on all candidates tested are as follows:

- Resins prepared under autoclave conditions employing a 505°K (450°F) cure temperature followed by a 589°K (600°F) postcure do not meet the 589°K ultimate long term stability objective of the program
- The BFBI/BMPM and 1500 FMW NE/MDA/BTDE candidates show promise for long-term use at 533°K (500°F) to 561°K (550°F) when initially processed (cured) at 505°K
- The DFQ/DMB candidate processed at 505°K cure/589°K postcure is unsuitable to meet minimum program stability objectives

A brief discussion of the results in terms of each candidate is presented in the paragraphs that follow.

The aging study on neat resin plugs definitely showed the BFBI/BMPM polymer candidate to be promising for use at 561°K. Apparently, this

TABLE XXIV

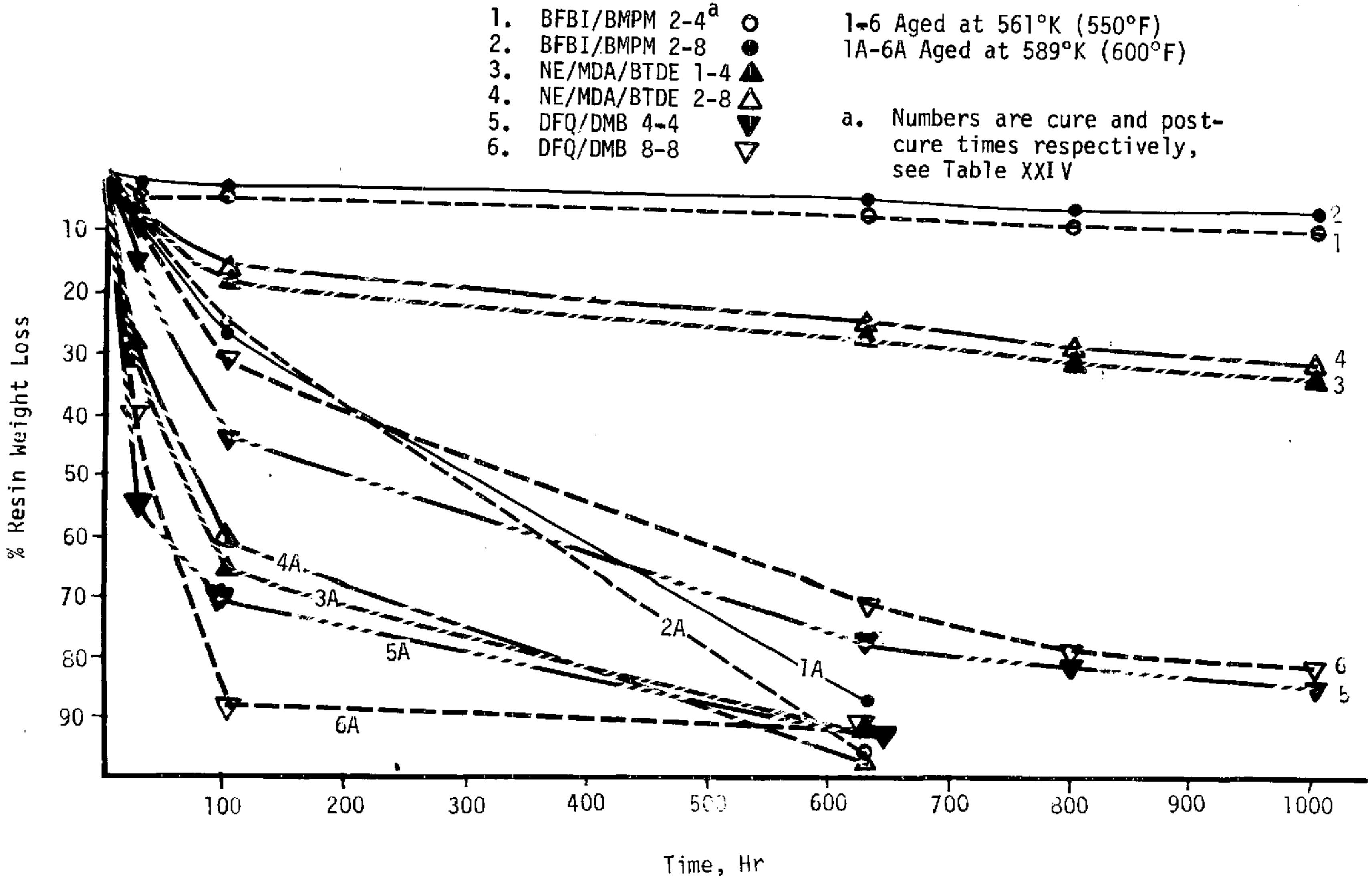
ISOTHERMAL AGING OF NEAT RESIN SAMPLES AT 561°K AND 589°K

Sample Composition	Cure and Postcure Conditions[a]		Weight Percent Loss - Duration Points in Hours									
			24 hr		100 hr		630 hr		800 hr		1000 hr	
	Cure,hr	Postcure,hr	561°K	589°K	561°K	589°K	561°K	589°K	561°K	589°K	561°K	589°K
BFBI/BMPM	2	4	2.87	12.71	4.38	27.79	7.31	86.88	8.00	b	9.49	b
BFBI/BMPM	2	8	1.79	11.43	2.76	26.76	4.65	96.93	5.93	b	6.41	b
NE/MDA/BTDE 1500 FMW	1	4	15.90	31.98	17.67	67.35	26.21	94.14	30.82	b	32.12	b
NE/MDA/BTDE 1500 FMW	2	8	8.06	28.18	18.19	60.45	25.66	99.61	29.28	b	31.41	b
DFQ/DMB	4	4	10.54	56.33	44.62	70.60	75.46	92.43	81.68	b	84.74	b
DFQ/DMB	8	8	7.63	40.56	31.18	88.24	71.51	91.65	79.30	b	82.55	b

[a] Other conditions; cure at 505°K, 1.4 MN/m^2; postcure conditions - 4 hour linear heat-up from 472°K to 589°K followed by isothermal cycle at 589°K for stated time.

[b] Not determined

FIGURE 11. Isothermal Aging of Neat Resin Samples at 561°K and 589°K



combination of ingredients is well suited for the PDA polymerization reaction under goal autoclave process conditions. In view of the excellent stability in air at 561°K, the system evidentally undergoes the postulated *in situ* aromatization reaction discussed in Section 3. Similar findings were observed in isothermal aging studies of HMS reinforced composites in Task III (see Section 4.2.3) and Task V (see Section 6), which demonstrated promising weight and mechanical property retention. This system is obviously worthy of further study.

The 1500 FMW NE/MDA/BTDE system, when subjected to initial cure of 505°K, then postcure at 589°K, is obviously not as well developed in thermoset character as when press-molded at temperatures of ≥561°K (Reference 5). It appears, as was shown for the bis(4-nadimidophenyl) methane (BNPM) and discussed in Section 2.4.1, that 505°K is approximately the minimum temperature at which the nadic end cap will undergo pyrolytic polymerization cure, induced by a reverse Diels-Alder reaction (References 1 and 3). From the shape of the weight retention curve at 561°K as plotted in Figure 11, degradation of some species, probably areas of incompletely cured polymer, occurs during the initial 24 hour to 100 hour exposure period, then the polymer matrix from that point out to the 1000 hour point gives a curve normally observed for the pyrolytically polymerizable polymers (i.e., 5% to 15% weight loss) at 561°K (References 1, 3 and 5). This behavior suggests that longer initial cure at 505°K (>2 hours) or additional postcure at ≥589°K may improve resistance to air at 561°K during initial exposure periods. The use of catalysts may help development of desired thermoset structures (Reference 1). However, mechanical properties retained by this system at 561°K are acceptable (see Section 6) and further work on this or similar PMR derived polymers is warranted.

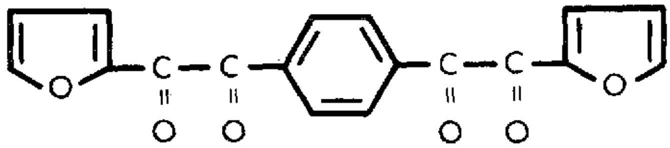
The failure of the DFQ/DMB system, as cured at 505°K and postcured at 589°K according to the conditions given in Table XXIV, was unexpected. This PDA derived polymer, void of oxidatively labile methylene linkages (see Section 5.1), should offer much better long-term thermo-oxidative stability than the BFBI/BMPM candidate at both 561°K and 589°K. Consequently, one must surmise that a 505°K cure temperature will not induce development of a high molecular weight matrix, thus making this polymer unsuitable for current program objectives. However, the high initial mechanical strengths demonstrated with HMS fiber reinforcement (see Section 5.2) do show that this candidate may give outstanding composites if higher process temperatures were employed.

5.1.5 Polyphenylquinoxaline Crosslink Experimentation

The PDA appraoch employing a quinoxaline-furan derivative such as DFQ suggested an interesting application of similar chemistry to achieve a viable polyphenylquinoxaline crosslinking reaction. A brief, significant study was conducted to demonstrate the applicability of PDA-type chemistry to achieve viable crosslinks in polyphenylquinoxaline (PPQ) resins. This study was based on the findings resulting from PDA modifications on the DFQ/DMB chemistry described above.

The thermo-mechanical stability of PPQ resin matrix systems has been well documented (e.g., Reference 11). However, the PPQ's employed to prepare graphite reinforced composites have shown that high temperature (i.e., 589°K) thermoplasticity of the linear resins preclude achievement of high temperature property retention. An approach to render the conventional PPQ system useful at high temperatures was investigated as based on a crosslinking mechanism to obtain a thermoset structure.

A new monomer, 1,4-bis(2-furylglyoxaloyl) benzene (BFGB), was prepared from furfural and terephthaldehyde (see Appendix C for experimental details). This tetracarbonyl compound shown below made it possible to prepare a PPQ which contained pendant furan groups. The furan groups



BFGB

allowed the same type of Diels-Alder cure mechanism as exhibited by DFQ/bis(maleimide) system to be utilized for crosslink formation.

A PPQ was prepared in 1:1 mixture of *m*-cresol/xylene from 50% m/m* 3,3-diaminobenzidine (DAB), 40% m/m *p*,*p*'-oxydibenzil (ODB) and 10% m/m of the TRW monomer BFGB. The linear PPQ containing the furan pendant groups was isolated by precipitation in methanol and dried *in vacuo*.

This linear polymer was subsequently treated with BMPM for one hour at 473°K (200°F) in *m*-cresol to give a gelled material, insoluble in the original *m*-cresol solvent. The polymer was also found to be insoluble in concentrated sulfuric acid giving added proof that the desired crosslinked structure had been obtained. This crosslinking mechanism offers the additional advantage fo being able to control the number of crosslinking sites through one of the monomers. Such control is of importance to obtain the maximum thermoset structure without introducing an excess of brittleness into the system.

It is strongly believed that the Diels-Alder-type cure of PPQ resins should be studied further. This or a similar approach may constitute a solution to the thermoplasticity problem of PPQ polymers.

5.2 COMPOSITE STUDIES

In order to investigate improved resins and/or processes over those studied in Task II and Task III, three distinct activities were performed:

- Evaluation of the DFQ/DMB resin system for preparing composites
- Evaluation of modified PMR resins for preparing composites
- Evaluation of modified BFBI/BMPM resins for preparing composites

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*m/m = mole percent

The results from these studies described herein indicated that the DFQ/DMB resin system was not suitable for processing within the constraints of this program. It was shown also that the PMR resin probably would process better at higher temperatures than were desired in this program (i.e., ~533°K). However, promising results were obtained with the BFBI/BMPM resin system particularly when this resin was used as an amide-acid solution for coating the graphite fiber reinforcement. These prepregs possessed good handlability at least equivalent to state-of-the-art polyimide resin prepregs. Autoclave cure of these prepregs was achieved under milder conditions [i.e., 472°K (390°F)] than the maximum program temperature objectives (i.e., 505°K). Details of the process studies are provided in the following paragraphs.

5.2.1 Preliminary Properties of DFQ/DMB HMS Composites

Due to the high initial promise shown by the DFQ/DMB system in the neat resin studies, a process study was initiated to obtain physical and/or mechanical properties utilizing HMS graphite. A brief cure matrix was accomplished to determine if the DFQ/DMB could be processed within the conditions of this program [i.e., >505°K (450°F) cure temperature, under 1.4 MN/m^2 (200 psi) cure pressure]. Cure times were varied from 2 hours to 16 hours at 505°K (450°F) with the cure pressure remaining at 0.7 MN/m^2 (100 psi). Panels cured 2 and 4 hours at 505°K (450°F), when removed from the vacuum bag exhibited excellent appearance. However, after postcure at 589°K (600°F) they were blistered (Table XXV). A staged postcure then was performed which provided some improvement but the composites still were unacceptable. The cure time in vacuum bag, therefore, was increased to 16 hours and the postcure was held at 8 hours at 589°K (600°F).

Preliminary properties obtained from the composite cured 16 hours at 505°K (450°F) were equivalent to the properties previously reported for the PMR resin (i.e. 1100 MN/m^2 flexural stress and 62 MN/m^2 shear strength). However, it was concluded at this point in time that higher cure temperatures than 505°K (450°F) are necessary to obtain sufficient cure before postcure. Consequently, this resin was unacceptable to meet the program objectives.

TABLE XXV

PRELIMINARY DFQ/DMB PROPERTIES

Post Cure Hrs/Temp°K	Cure Time Hours @ 505°K	Mechanical Properties Flexural Strength(1) MN/m^2	Short Beam Strength(2) MN/m^2
8/591	2	(3)	(3)
16/591	5	(3)	(3)
8/519 16/547 4/591	5	(3)	(3)
8/591	16	1118 (160 ksi)	62.4 (8.9 ksi)

(1) Flexural span was 32 times specimen thickness.
(2) Specimen span was 4 times specimen thickness. Specimen length was 6 times specimen thickness.
(3) Panels exhibited varying degrees of blisters and were not tested.

5.2.2 PMR Process Studies

Work was continued in developing a process for making composites from PMR resins utilizing the promising NE/MDA/BTDE (1500 FMW) formulation modified by the addition of a thixotropic agent. During Task III (Section 4), the difficulty in processing this resin by accepted autoclave molding techniques was identified as fiber washout caused by the loss of resin during the "A" and/or "B" staging of the composites. The most probable cause was determined to be the low viscosity of the combination of monomer/residual solvent during the "A" and/or "B" stages.

One of the approaches to correct this problem was the evaluation of a thixotropic agent (Cab-O-Sil). This was evaluated at concentrations of 1 and 3% w/w of resin solids and the results (see Table XX) from this study identified two further problems:

a) at 1% w/w level the resin flow was too high in the "A" and/or "B" stages.

b) at 3% w/w level the resin flow was reduced in the "A" and/or "B" stages but no flow occurred after imidization which resulted in poor consolidation and high void contents.

TABLE XXVI

NE/MDA/BTDE FLOW STUDIES

Prepreg Properties				Laminate Properties(1)				
Formula Molecular Weight	Volatile Matter % w/w (2)	Resin Content % w/w	Filler Level % w/w	Resin Flow % w/w (3)	Resin Content % w/w	Density g/cc (4)	Flexural Strength @ R.T. (5) MN/m^2	Shear Strength @ R.T. MN/m^2 (6)
1500	17.0	50.0	3	1.8	7	7	7	7
1500	12.9	42.7	1	9.5	35.5	1.571	753	40.2
2000	13.0	48.0	-	11.0	7	7	7	7
2500	13.0	39.6	-	4.2	7	7	7	7

(1) Cure cycle: pull vacuum, raise temperature to 350°K for 1 hour and then to 395°K for 1 hour. Apply 0.7 MN/m^2 (100 psi) positive pressure and raise to 505°K (450°F) for 4 hours. Cool under vacuum. Postcure 4 hours at 589°K (600°F).

(2) Volatile matter content determined by measurement of weight loss after 30 minutes at 560°K (550°F)

(3) Resin flow calculation: $\frac{\text{Weight loss of composite during cure}}{\text{Dry weight of composite before cure}} \times 100$

(4) Density determined per ASTM D792-66

(5) Testing span was 32 times specimen depth

(6) Testing span was 4 times specimens depth. Specimen length was 6 times specimen depth

(7) Panel of poor quality and no tests were conducted

The final approach used was to vary the formulated molecular weight of the NE/MDA/BTDE in order to control resin flow (the FMW's chosen were 2000 and 2500). Graphite tapes and composites were manufactured (Table XXVI) from these resins. As can be seen, no improvement in properties were observed and the resultant panels were of very poor quality even though the flow was reduced. Consequently, these resin systems were deemed not suitable for further evaluation because of the lack of panel consolidation.

These processing difficulties are absent in the highly promising press laminate fabrication of PMR resin/graphite composites (Reference 5). Consequently, the lack of desired behavior of the NE/MDA/BTDE resin in Task III is ascribed to the initial methodology used to adapt this formulation to significantly different autoclave molding process cycles.

It was decided to approach the "fiber-washout" problem by imidizing the graphite tape prior to the autoclave cycle. Two separate methods were evaluated to accomplish the partial imidization: a) prestack the prepreg and then partially imidize and b) partially imidize the graphite tape. The first approach (i.e., prestacking the graphite tape) proved unsuccessful because the large amount of solvent present in the tape blistered the preform and disorientated the graphite fibers. However, the second method (i.e., partially imidizing the graphite tape) proved to be more successful and after preliminary screening, a satisfactory drying cycle was developed which gave a graphite tape that was processed into acceptable composites.

A detailed process screening study similar to the one previously employed for the PDA prepregs was initiated. This study included a fractional factorial experiment with five processing variables. The parameters evaluated during the study were the rate of temperature rise to cure temperature, cure pressure, initial postcure temperature, final postcure temperature and final postcure time. Two levels of each of the above conditions, selected on the basis of data from the Audrey II scans and results of previous experiments, were evaluated as shown in Figure 12. The cure conditions for this study were 4 hours at 505°K (450°F). It also was determined in this study that a step postcure was essential to give composites of low void volume. Without the step postcure, composites of

Figure 12. Processing Studies Matrix

Expt	Factors/Condition[a]				
	A	B	C	D	E
1	-	-	-	-	-
2	+	-	-	+	-
3	-	+	-	+	+
4	+	+	-	-	+
5	-	-	+	+	+
6	+	-	+	-	+
7	-	+	+	-	-
8	+	+	+	+	-

a) Code for factors/conditions matrix

Factor		+	-
A	Temperature rate of rise	5.0-5.6°K/min.	2.3-3.3°K/min
B	Cure Pressure	0.7 MN/m^2	1.05 MN/m^2
C	Initital Postcure Temperature	533°K	547°K
D	Final Postcure Temperature	589°K	615°K
E	Final Postcure Time	4 hours	8 hours

high void content (>10% void volume) were obtained. The most probable cause of the high void content composites was attributed to the rapid evolution of cyclopentadiene during postcure. The information desired from this matrix were the main effects of the variables and the major first order interactions. The physical and mechanical properties subsequently were determined on composites fabricated by using the simulated autoclave molding arrangement and with processing conditions defined in the above matrix (see Figure 12). In addition to the room temperature property determinations, flexural strengths at 589°K (600°F) also were determined (see Table XXVII). A statistical analysis was performed using techniques described by Davies (Reference 9) and the results are given in Tables XXVIII through XXX.

TABLE XXVII

SUMMARY DATA CURE STUDY

Autoclave Cycle		Postcure Cycle			Laminate Physical Properties				Laminate Mechanical Properties		
Temp Rate of Rise °K/min.	Pressure MN/m^2	Initial Temp °K (1)	Final Temp °K	Final Time Hrs.	Resin Content % w/w	Density g/cc (2)	Void Vol. % v/v (5)	Fiber Vol. % v/v (6)	Flexural Strength MN/m^2 (3)	Short Beam Shear Strength MN/m^2 (4)	Test Temp °K
5/6	0.7	533	589	4	38.7	1.57	4.3	49.0	918 898	48.3	295 589
9/10	0.7	533	615	4	37.0	1.53	7.3	49.2	842 1014	46.7	295 589
5/6	1.05	533	615	8	36.3	1.53	7.5	49.7	1135 1297	49.8	295 589
9/10	1.05	533	589	8	39.5	1.57	2.9	49.1	944 1209	46.3	295 589
5/6	0.7	547	615	8	33.7	1.58	5.8	53.3	978 1015	66.8	295 589
9/10	0.7	547	589	8	35.6	1.56	6.0	51.3	1083 1504	64.0	295 589
5/6	1.05	547	589	4	38.0	1.57	4.4		1028 1339	50.7	295 589
9/10	1.05	547	615	4	34.3	1.58	5.5	52.9	1060 1083	64.8	295 589

(1) Panel postcured 16 hours at temperature

(2) Density was determined with following formula: $\frac{\text{Specimen Weight in Air}}{\text{Specimen Weight in Air} - \text{Specimen Weight in } H_2O}$

(3) The test span was determined by multiplying the specimen thickness by 32

(4) The specimen length was 6 times specimen thickness and test span was 4 times specimen thickness

(5) Calculated from resin content and measured density values

(6) Calculated from resin content value

TABLE XXVIII
STATISTICAL ANALYSIS OF R.T. SHEAR STRENGTHS

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Mean Square (Col 2)^2/8
A,-DE	6.2	1.55	1	4.81
B,-CE	-14.2	-3.55	1	25.21
C,-BE	55.2	13.80	1	308.88
D,-AE	18.8	4.70	1	44.18
E,-AD,-BC	16.4	4.10	1	33.62
AB,CD	15.0	3.75	1	28.13
AC,BD	16.4	4.1	1	36.62

TABLE XXIX
ANALYSES OF 589°K FLEXURAL STRENGTH

Comparison	Total	(Col 2)/4	Degree of Freedom	Mean Square (Col 2)^2/8
A,-DE	261	65.25	1	8,515
B,-CE	497	124.25	1	30,876
C,-BE	523	130.75	1	34,191
D,-AE	-541	-135.25	1	36,585
E,-AD,-BC	691	172.75	1	59,685
AB,CD	-949	-237.25	1	112,575
AC,BD	205	51.25	1	5,253

TABLE XXX

STATISTICAL ANALYSES OF R.T. FLEXURAL STRENGTH

Comparison	Total	Effect (Col 2)/4	Degree of Freedom	Mean Square $(Col\ 2)^2/8$
A,-DE	-130	-32	1	2,113
B,-CE	346	86.5	1	14,965
C,-BE	310	77.5	1	12,013
D,-AE	42	10.5	1	221
E,-AD,-BC	292	73.0	1	10,658
AB,CD	404	101	1	20,402
AC,BD	-188	-47.0	1	4,418

Analysis of room temperature shear properties (Table XXVIII), room temperature flexural properties (Table XXX) and 589°K (600°F) flexural strengths (Table XXIX) indicated factor C,-BE could be significant. Analyses of room temperature and 589°K (600°F) flexural strengths (Tables XXX and XXIX, respectively) indicated that factors AB, CD; B,-CE and E,-AD, -BC also to be significant. The data presented in Table XXIX shows that higher elevated temperature retention could be obtained with the 589°K (600°F) postcure temperature. Based on past experience and the information derived from this matrix design, the following cure cycle shown below was selected as being the most promising to produce graphite composites possessing satisfactory mechanical properties utilizing the PMR system.

Cure Temperature	505°K (450°F)
Cure Time	4 hours
Rate of Temperature Rise	2.9-3.3°K/minute
Cure Pressure	0.7 MN/m^2
Initial Postcure Temperature	547°K (525°F)
Initial Postcure Time	16 hours
Final Postcure Temperature	589°K (600°F)
Final Postcure Time	8 hours

Photomicrographs were taken of the highest shear strength composites (Figure 13) indicating excellent fiber distribution. There is no evidence of macrovoids (i.e., voids >50 microns) with the bulk of the voids in the range of 5-10 microns in diameter.

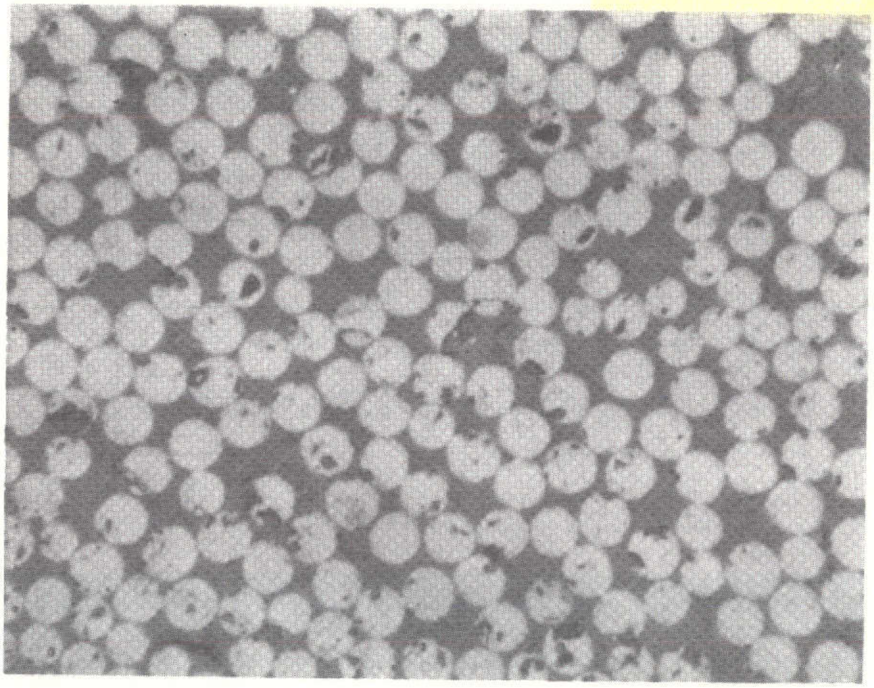

Figure 13. Photomicrograph of 1500 FMW NE/MDA/BTDE Composite (800X)

Attempts were then made to mold 20-cm by 20-cm square panels but with unsatisfactory results. Severe blistering occurred during postcure of these panels and consequently, it was concluded that a higher cure temperature of up to 533°K (500°F) may be necessary for routine processing of this resin system. This approach was not pursued because one of the key objectives of the program was to obtain initial resin cure below 505°K. It is most probable that the blistering was caused by evolution of cyclopentadiene, not effectively incorporated into the resin matrix (see Section 3.3 for similar observations).

5.2.3 BFBI/BMPM Process Studies

During Task III studies, the major deficiency identified for the BFBI/BMPM resin system was its propensity to precipitate out of solution on the prepreg tape. Consequently, it was decided to address this particular problem during the Task IV activities. The approach taken to resolve this problem was to impregnate the Hercules HMS graphite fibers with an amide-acid solution of the BFBI/BMPM resin (the monomers are prepared initially as the amide-acid - see Appendix B). Prepregs prepared in this manner possessed excellent handling characteristics, therefore, autoclave molding studies were commenced.

Composites were molded using a similar process to that used previously during Task III. These composites showed high promise but possessed high void content. Therefore, a longer staging cycle then was employed which provided a significant improvement to lower void content and give acceptable mechanical properties (see Table XXXII in Section 6). Consequently, this process, as given in Appendix D, was employed for preparing composites for Task V detailed evaluations.

6. TASK V - DETAILED EVALUATION

Composite panels were autoclave molded containing PMR resin (NE/MDA/BTDE 1500 FMW) or PDA resin (BFBI/BMPM) with Hercules HMS high modulus graphite fiber reinforcement using the procedures defined in Task IV (see Sections 5.2.2 and 5.2.3, respectively). These panels were employed to give flexural and shear specimens for determination of mechanical and physical properties before and after isothermal aging at 561°K (550°F) and 589°K (600°F). Details of this work are provided below.

6.1 TEST PROCEDURES

The PMR and PDA graphite composite panels were machined into flexural and short beam shear test specimens. Dimensions of the flexural specimens were 0.6 cm by 7.6 cm by .02 cm and the short beam shear specimens were 0.6 cm by 1.2 cm by .02 cm. Test specimens for isothermal aging evaluations were weighed and placed on metal shelves in two air circulating ovens each with an air velocity of 12.7 m/sec and an air change rate of 19.7 m^3/sec. Air temperature in the two ovens was stabilized at the aging temperature, i.e., 561°K (550°F) and 589°K (600°F). Specimens were withdrawn from the air circulating ovens after aging durations of 100, 300, 500 and 1000 hours and placed in a desicator. Flexural and shear properties were determined on as-molded and isothermally aged specimens in accordance with the procedures defined in Appendix E. Weight loss calculations were made on the isothermally aged specimens and resin retention plots were made.

6.2 TEST RESULTS

Flexural and shear properties (see Table XXXI) of the unaged PMR/HMS graphite composite specimens were lower than those obtained previously with press-molded PMR/HMS graphite composite panels (Reference 7). These low properties are attributed to an incomplete initial cure during the autoclave molding cycle. The isothermal aging resin degradation rate was comparable with other similar polyimide resins (see Table XXXI and Figures 14 and 15) as were the mechanical properties degradation rates (see Figures 16 through 18). These data correspond with the findings at NASA Lewis Research Center (Reference 5) for press molded PMR resin composites.

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TABLE XXXI

ISOTHERMAL AGING PROPERTIES OF PMR/HMS GRAPHITE COMPOSITES

Aging Temp. °K	Aging Temp. Hrs.	Test Temp. °K	Weight Loss		Mechanical Properties					
			S.B. Shear Spec.	Flexural Specimen	Flexural Strength	MN/m^2 (Ksi)	Flexural Modulus	GN/m^2 (msi)	Short Beam Shear Strength	MN/m^2 (Ksi)
561	0	295	-	-	811	(115.4)	16.9	(24.0)	41.3	(5870)
		561			578	(82.2)	15.2	(21.6)	30.7	(4370)
561	100	295	1.02	2.13	809	(115.1)	15.8	(22.5)	36.2	(5150)
		561			671	(95.5)	15.1	(21.3)	26.5)	(3770)
561	300	295	5.73	4.53	777	(110.5)	20.0	(28.4)	31.5	(4480)
		561			640	(91.1)	16.2	(23.1)	27.4	(3900)
561	500	295	7.50	6.46	857	(121.9)	18.1	(25.8)	31.3	(4450)
		561			661	(94.0)	18.8	(26.7)	28.1	(4000)
561	1000	245	9.53	9.37	767	(109.1)	16.5	(23.4)	30.2	(4300)
		561			622	(88.4)	23.1	(32.8)	27.4	(3900)
589	0	295	-	-	811	(115.4)	16.9	(24.0)	41.3	(5870)
		589			725	(103.2)	16.9	(24.1)	35.5	(5050)
589	100	295	4.85	3.19	795	(113.1)	16.9	(24.0)	33.7	(4800)
		589			647	(92.4)	15.7	(22.3)	30.0	(4270)
589	300	295	8.27	6.30	723	(102.9)	17.8	(25.3)	27.0	(3840)
		589			640	(91.1)	16.2	(23.1)	27.4	(3900)
589	500	295	9.57	8.23	736	(104.7)	17.9	(25.5)	23.7	(3370)
		589			582	(82.8)	18.5	(26.3)	22.0	(3130)
589	1000	295	15.48	12.90	594	(84.4)	18.0	(25.6)	15.0	(2130)
		589			552	(78.9)	15.7	(22.3)	12.7	(1800)

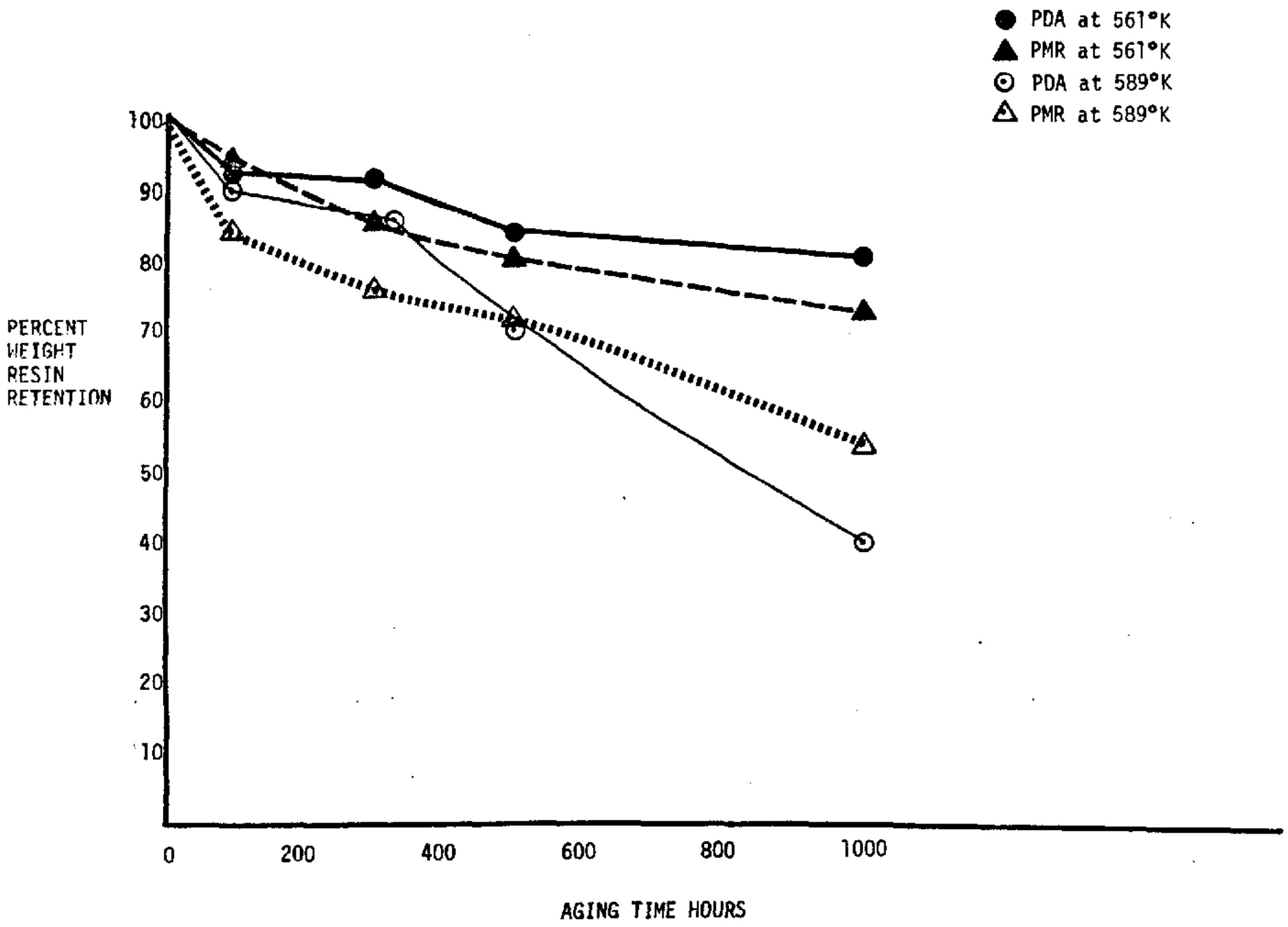

Figure 14. Plot of Resin Weight Retention of PMR and PDA Short Beam Shear Specimens as a Function of Isothermal Aging at 561°K and 589°K

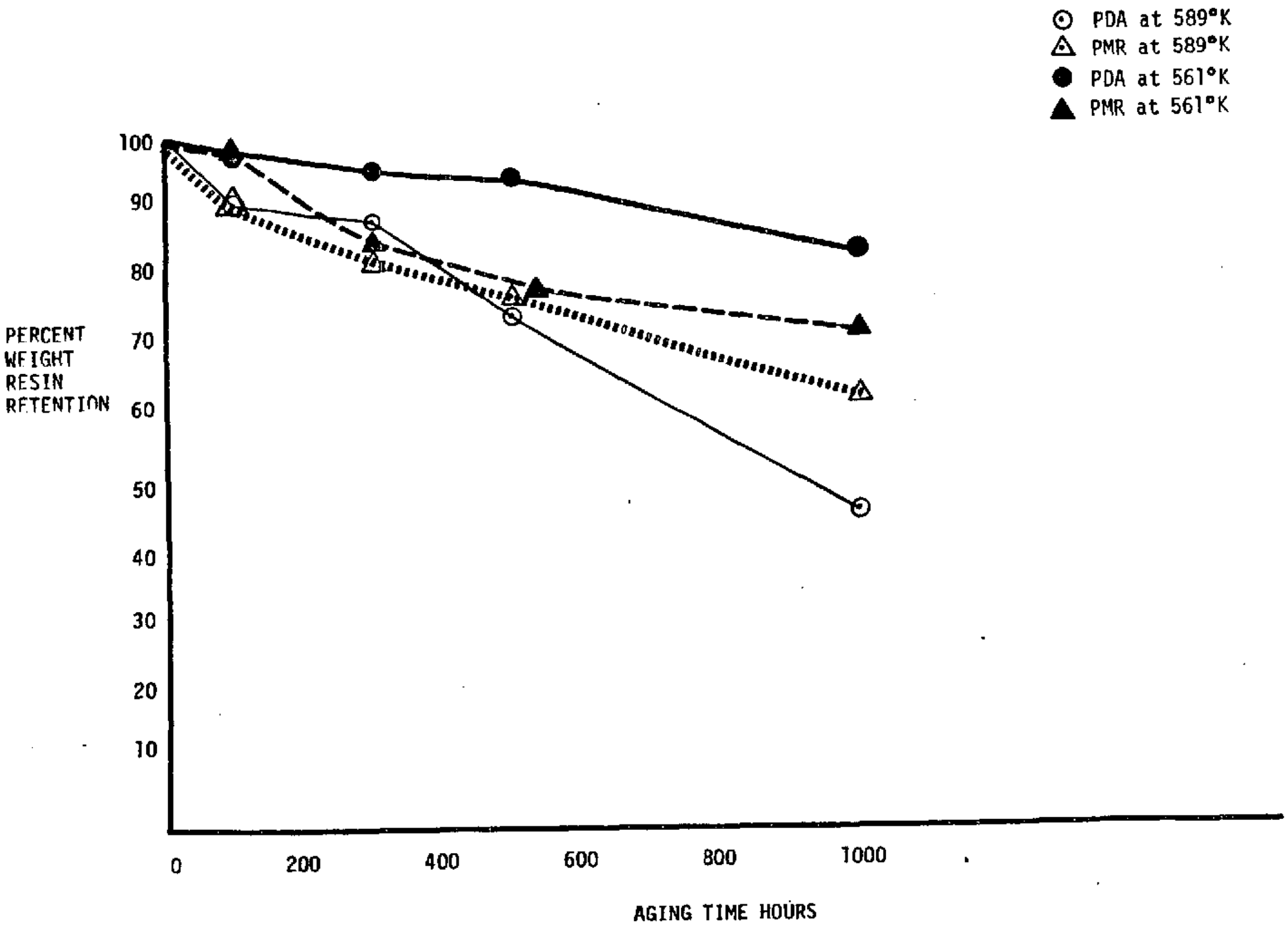

Figure 15. Plot of Resin Weight Retention of PMR and PDA Flexural Specimens as a Function of Isothermal Aging at 561°K and 589°K

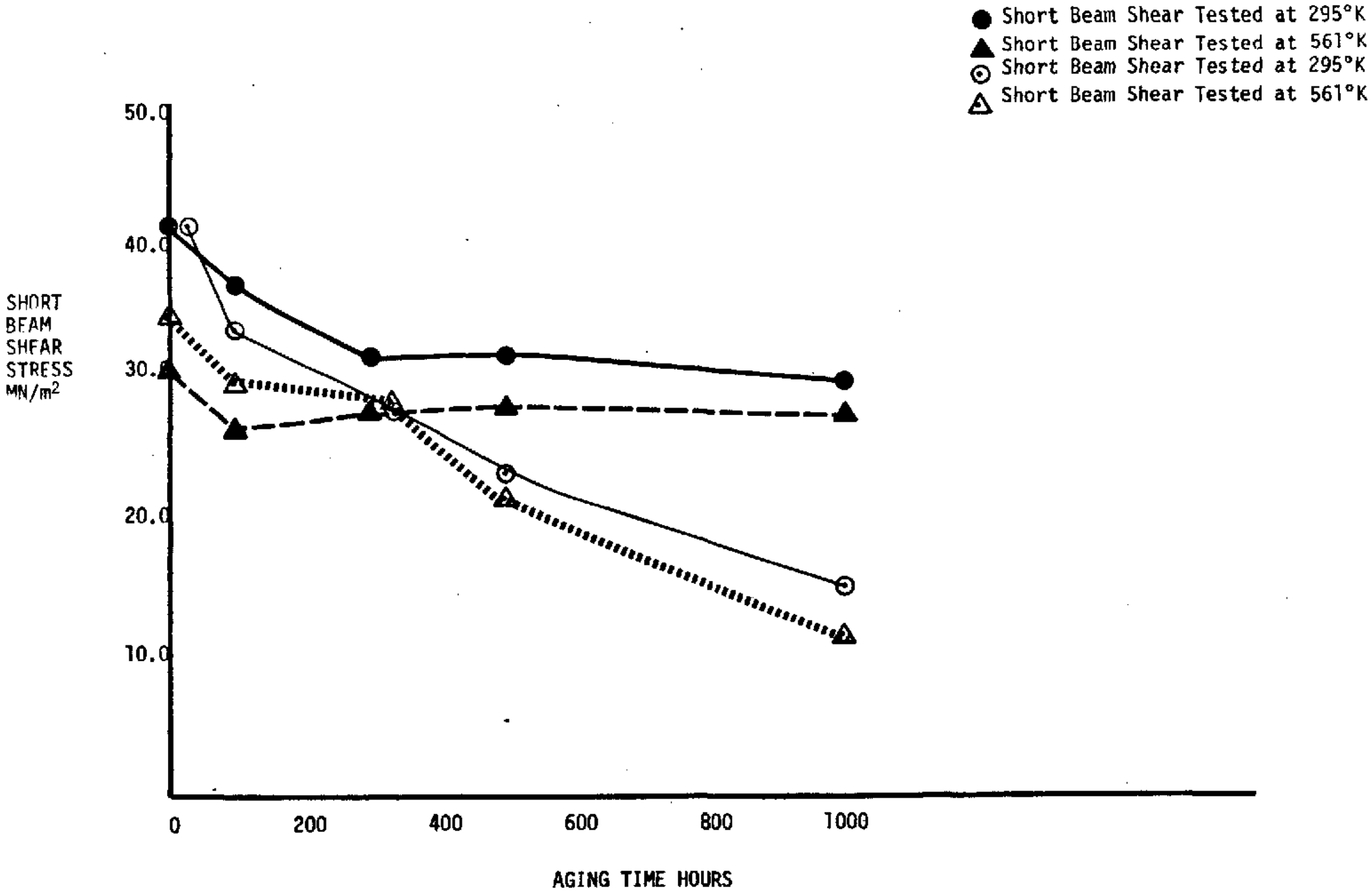

Figure 16. Plot of PMR Short Beam Shear Strength as a Function of Isothermal at 561°K and 589°K

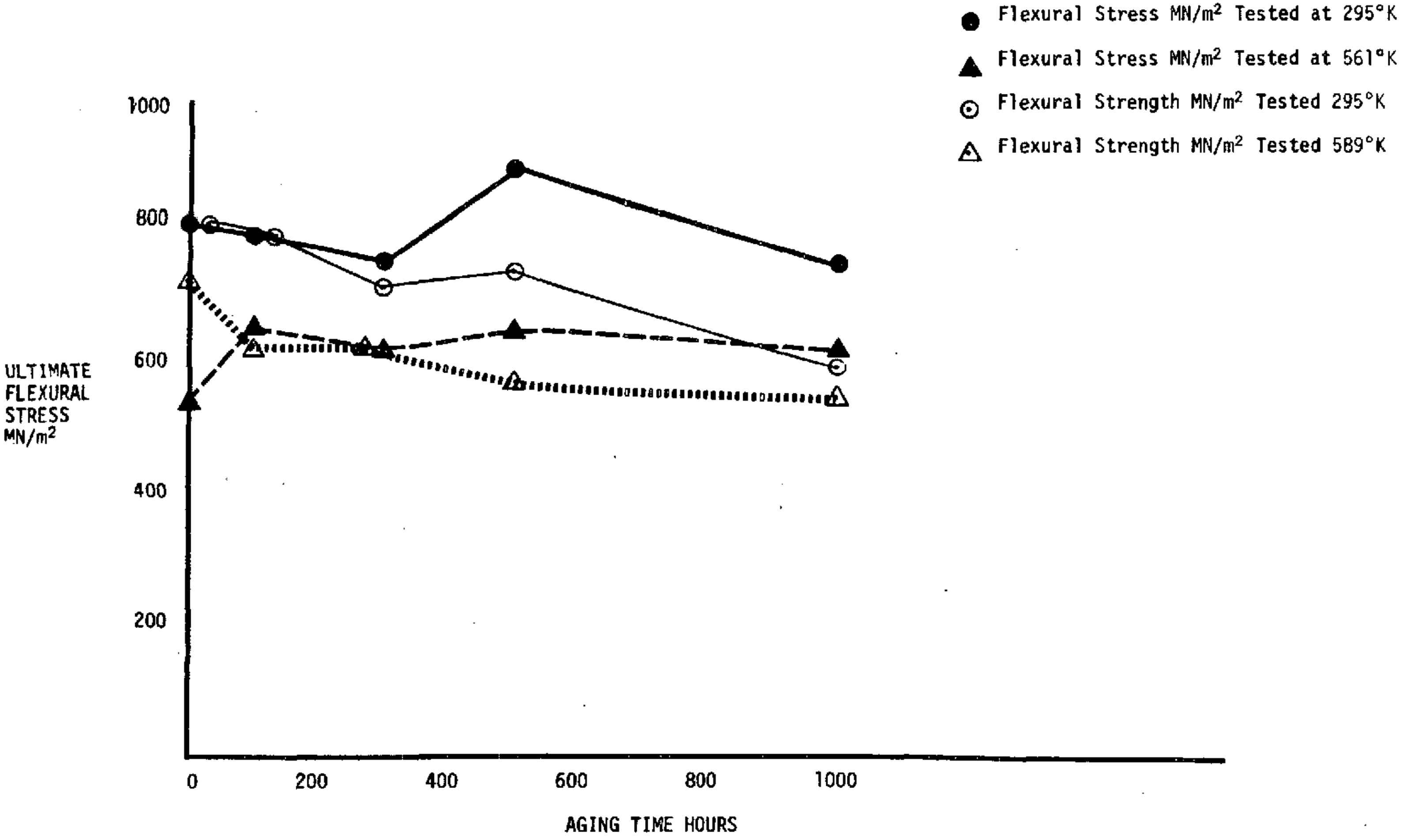

Figure 17. Plot of PMR Flexural Strength as a Function of Isothermal Aging at 561°K and 589°K

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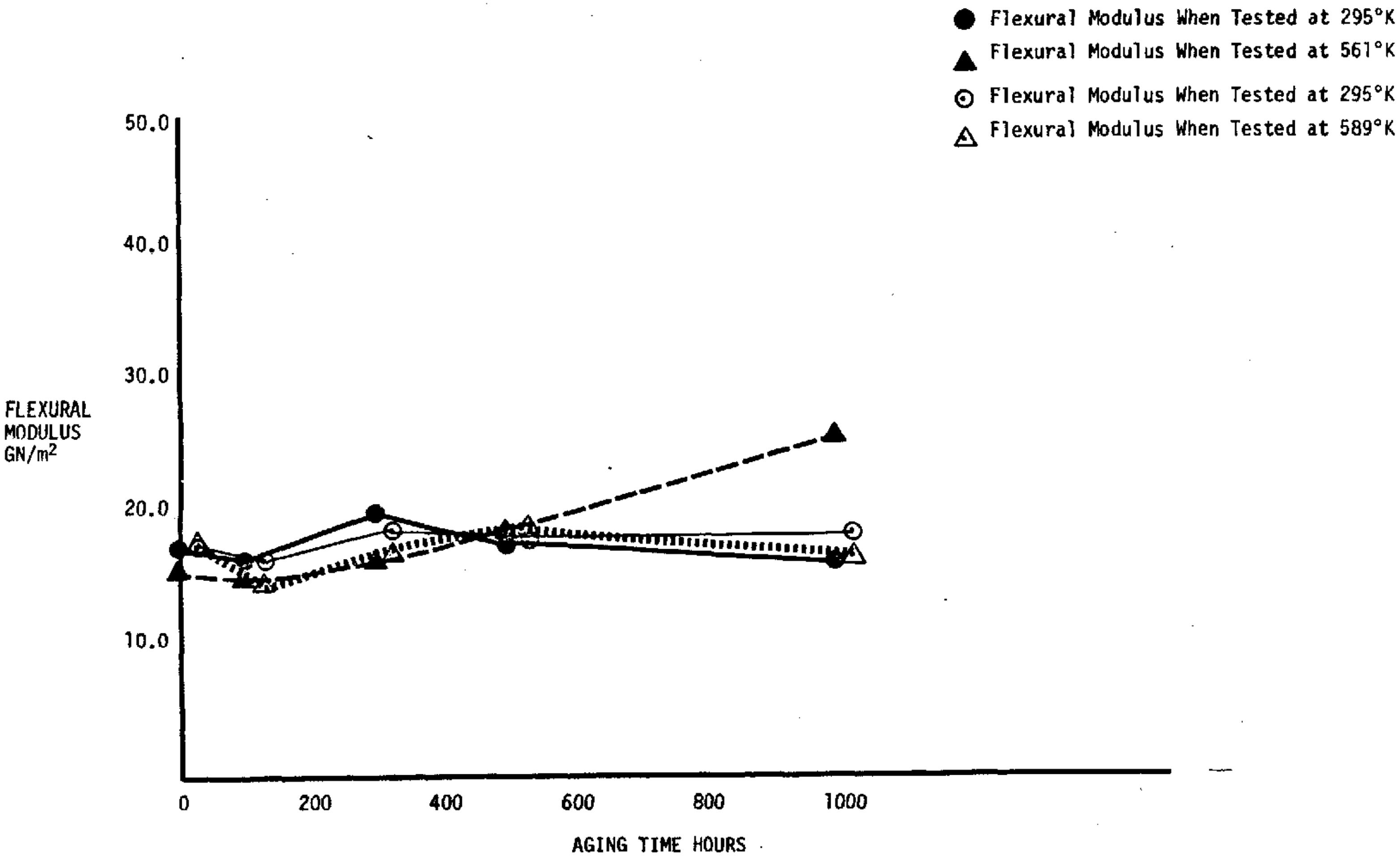

Figure 18. Plot of PMR Flexural Modulus as a Function of Isothermal Aging at 561°K and 589°K

The initial properties of the unaged PDA/HMS graphite composite specimens were comparable with press molded P13N composites (see Table XXXII) thus indicating that an acceptable initial cure is obtained at 473°K (390°F). Also, the resin degradation rate, as determined by weight retention after isothermal aging, was equivalent to other polyimide resins (see Figures 14 and 15). Corresponding properties retention also were obtained after isothermal aging for 500 hours at 561°K and 589°K (see Figures 19 and 20). These results were interpreted to mean that the PDA resin is suitable for processing under mild conditions [i.e., 473°K (390°F) cure temperature and 0.7 MN/m^2 (100 psig) molding pressure].

However, after a 1000-hour aging duration at 589°K, the PDA composites demonstrated a significantly higher degradation rate than the PMR composites. Degradation rates for both PDA and PMR composites were similar to each other at 561°K. Therefore, it was concluded from these results that the PDA resin is suitable for long-term service at 561°K and that the PMR resin is suitable for long-term service at 589°K. The significant processing difference between these two resin systems is that the PDA resin can be cured at ∿473°K (390°F) and the PMR resin requires 505°K (450°F) minimum cure temperature.

TABLE XXXII

ISOTHERMAL AGING PROPERTIES OF PDA/HMS GRAPHITE COMPOSITES

Aging Temp. °K	Aging Time Hrs.	Test Temp. °K	Weight Loss		Mechanical Properties					
			S. B. Shear Specimen	Flexural Specimen	Flexural Strength MN/m²	(Ksi)	Flexural Modulus GN/m²	(msi)	Short Beam Shear Strength MN/m²	(Ksi)
561	0	295	-	-	1206	(171.7)	21.3	(30.3)	33.3	(4730)
		561			455	(64.7)	13.8	(19.7)	19.7	(2800)
561	100	295	1.99	1.01						
		561			560	(79.6)	18.1	(25.8)	29.0	(4130)
561	300	295	2.06	1.45						
		561			643	(91.4)	19.4	(27.6)	26.6	(3780)
561	500	295	4.20	2.17	468	(66.6)	19.0	(27.0)	29.5	(4200)
		561								
561	1000	295	4.9	4.3	464	(66.0)	19.1	(27.2)	21.1	(3000)
		561								
589	0	295	-	-	1206	(171.7)	21.3	(30.3)	33.3	(4370)
		589			354	(50.3)	14.1	(20.1)	14.8	(2100)
589	100	589	2.34	2.41	642	(91.3)	18.1	(25.8)	24.6	(3500)
589	300	589	3.56	3.17	528	(75.1)	19.1	(27.2)	23.2	(3300)
589	500	589	6.95	6.55	502	(71.4)	18.4	(26.1)	29.7	(2800)
589	1000	295	14.8	13.6	148	(21.0)	13.2	(18.8)	14.7	(2100)
		589								

1 = $\frac{\text{Strength at Test Temp}}{\text{Strength at 295°K}}$ X 100

2 = $\frac{\text{Strength After Aging}}{\text{Strength of Control}}$ X 100

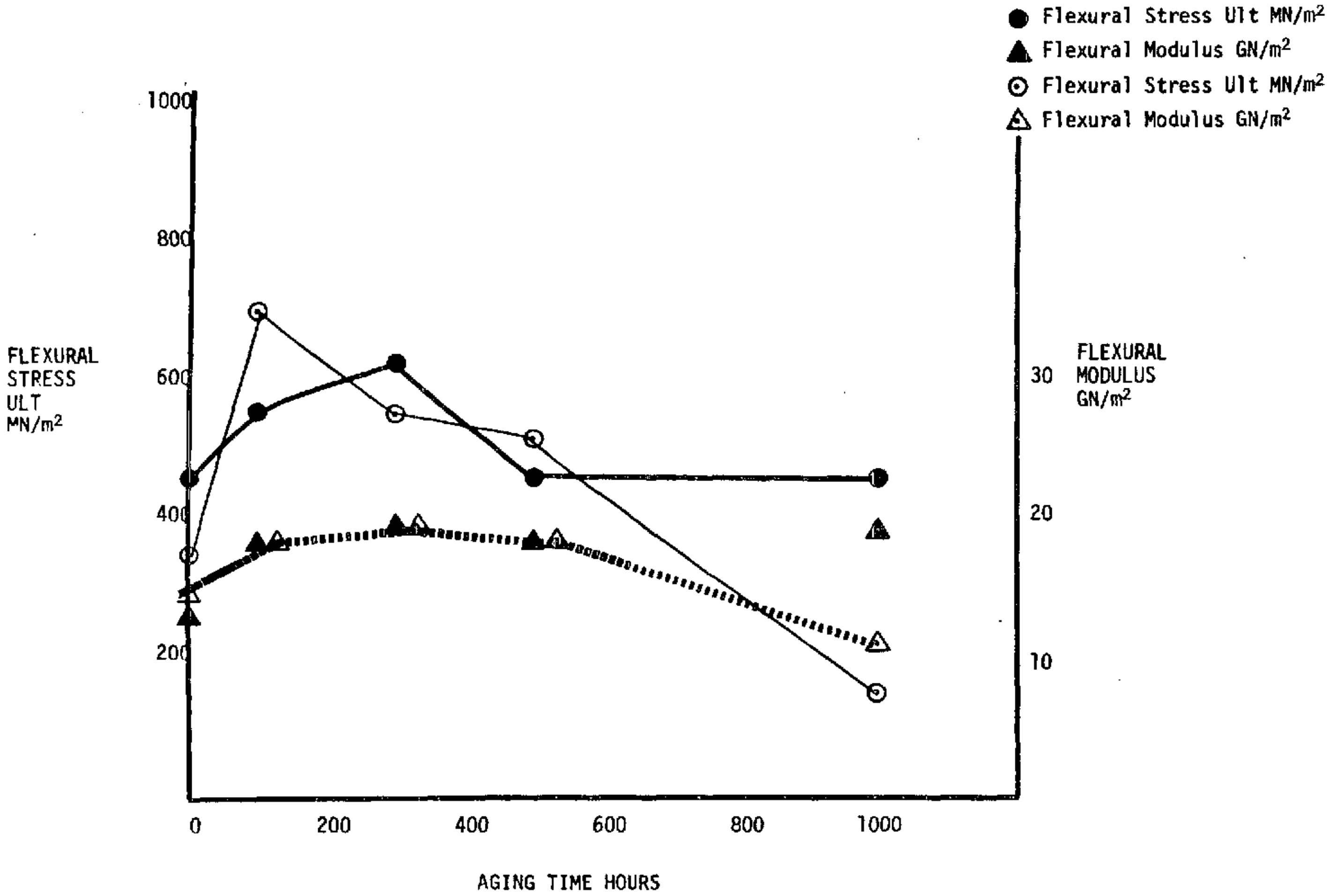

Figure 19. Plot of PDA Flexural Strength and Modulus as a Function of Isothermal Aging at 561°K and 589°K

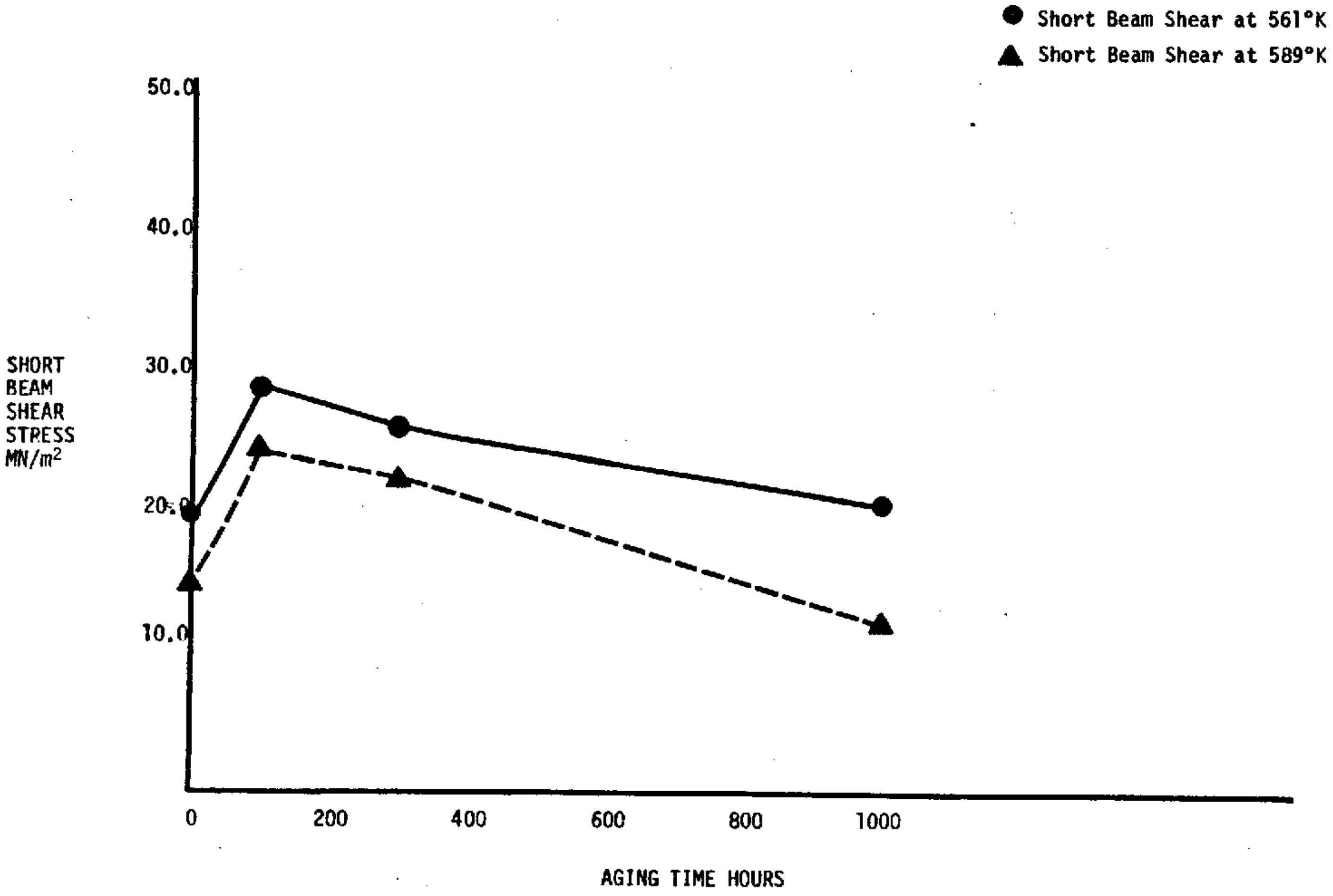

Figure 20. Plot of PDA Short Beam Shear Strength as a Function of Isothermal Aging at 561°K and 589°K

VII. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental study to define addition-type polyimides suitable for preparation of high performance composites by an autoclave process at temperatures $\leq 505°K$. Based on the findings, recommendations are given for further material and process improvement studies.

7.1 CONCLUSIONS

1. Model compound studies have provided considerable insight into temperatures required to effectively induce pyrolytic polymerization of end caps possessing a norbornene (nadic)-type structure; it was shown that nadic anhydrides will undergo such a reaction at an approximate minimum temperature of 505°K (450°F).
2. Polymer studies have shown that polymerization of monomeric reactants (PMR) and poly(Diels-Alder) approaches are suitable addition-type routes to achieve autoclave composite fabrication at temperatures of 505°K or less.
3. A combination of monomethyl nadic ester (NE), methylene dianiline (MDA) and the dimethyl ester of benzophenone tetracarboxylic acid (BTDE) at a stoichiometry level designed to yield a 1500 g/mol formulated molecular weight (FMW) polymer as prepared by PMR methodology was identified as a promising candidate suitable for autoclave fabrication of high performance HMS-reinforced composites at goal process parameters [temperature = 505°K; pressure = 0.7 MN/m^2 (100 psi); duration = 2 hours].
4. A combination of bis(furfuryl) benzophenone tetracarboxylic imide (BFBI) and bis(4-maleimidophenyl) methane (BMPM) as prepared by poly(Diels-Alder) (PDA) methodology was identified as a promising candidate for autoclave fabrication of high performance HMS-reinforced composites at process parameters [temperature = 473°K (390°F); pressure = 0.7 MN/m^2; duration = 2 hours].

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5. A postcure cycle of four hours at 589°K (600°F) was shown to be effective for final staging of HMS composites prepared from both the PMR and PDA approaches.
6. The PDA-type chemistry can be employed as a novel route to crosslink polyphenylquinoxaline resins.
7. HMS reinforced composites prepared by the autoclave processes summarized in 3, 4, and 5 above, are suitable for long-term ($\geq$1000 hours) use in air at 561°K (550°F); the same composites behave similarly to P1OP-A discovered in Contract NAS3-13489 on isothermal exposure to air at 589°K (long-term use is limited to $\leq$1000 hours).

7.2 RECOMMENDATIONS

1. Model studies should be conducted to define the precise temperature range at which the postulated *in situ* aromatization of the PDA polymer occurs and to what degree as a function of temperature; the results should be used to define a minimum practical temperature for autoclave cure.
2. Variations in formulated molecular weights should be investigated for the PMR approach to optimize processability/property trade-offs for autoclave cure at 505°K (450°F).
3. Variations in ingredient formulary should be investigated for the PDA approach to optimize processability/property tradeoffs for autoclave cure at 422°K (300°F) to 477°K (400°F); studies should be conducted on the effect of crosslink density on 533°K (500°F) to 589°K (600°F) initial and retained mechanical properties.
4. Postcure studies should be conducted on promising PMR and PDA derived resins and should include temperatures and durations as variables.
5. Initial composite data should be obtained on selected polyphenylquinoxaline resins crosslinked by Diels-Alder chemistry

to assess initial and long-term mechanical property characteristics in air at 589°K to 644°K (700°F).

6. Resin synthesis/fabrication process reproducibility studies should be conducted on the most promising PMR and/or PDA candidates.

7. Detailed property assessment should be conducted on the most promising resin system and should include study of severe environmental effects at low, intermediate and high temperatures.

VIII. NEW TECHNOLOGY

This section provides discussions of new methods developed during this program to prepare HMS-type high modulus graphite reinforced composites by autoclave processes together with new compositions of matter and a novel method of crosslinking polyphenylquinoxalines. These concepts are believed to be of sufficient novelty that invention disclosures have been submitted to the TRW Patent Office. The subject of these disclosures are listed below:

DOCKET NO.	TITLE
73-108	Fabrication of High Performance Composites Employing a PMR or PDA Derived Resin and an Autoclave Process
73-106	New Bis(benzil) Composition of Matter
73-107	A Novel Method for Crosslinking Polyphenylquinoxalines Resins
73-103	Quinoxaline-Imide Compositions of Matter

A separate report covering these disclosures has been submitted to the NASA/LeRC Technical Utilization Officer. Brief discussions of these disclosures, their novelty, features and applications are presented below.

8.1 FABRICATION OF HIGH PERFORMANCE COMPOSITES EMPLOYING A PMR OR PDA DERIVED RESIN AND AN AUTOCLAVE PROCESS

A process for preparing HMS graphite reinforced composites employing a PMR monomer composition consisting of the monomethyl ester of nadic anhydride, methylene dianiline and the dimethyl ester of benzophenone tetracarboxylic acid at a formulated molecular weight of 1500 g/mol (1500 FMW NE/MDA/BTDE) suitable for autoclave fabrication was developed. The preferred process consists of impregnation of fiber with the resin at $\sim$2.5% volatiles and 35-38% w/w resin content suitable for lay-up and cure. The prepreg then is cut to the desired length and width dimensions and several plies are stacked to effect a proper thickness. This prepreg configuration then is bagged employing Kapton film and introduced into an autoclave. The lay-up is cured employing a process cycle of raising the temperature to

505°K (450°F) at the rate of 4°K/min (7°F/min) under 1.1 MN/m^2 (150 psi), curing for 4 hours at 505°K and then cooling under vacuum bag pressure. The partially cured composite product of high mechanical integrity then is placed in an air-circulating oven and postcured employing a staged cycle consisting of 16 hours at 547°K (525°F) followed by 8 hours at 589°K (600°F). The finished composite prepared by this total process possesses an excellent combination of properties [e.g., 3-5% voids, 900 MN/m^2 (130 Ksi) flexural strength and 41 MN/m^2 (6 Ksi) short beam shear strength]. An average of 70% of the mechanical strengths are retained initially on testing at 589°K (600°F). The composite products are suitable for long-term use in air at 561°K to 589°K (550°F to 600°F).

A process for preparing HMS graphite reinforced composites employing a PDA monomer composition consisting of bis(4-maleimidophenyl) methane (BMPM) and bis(furfuryl) benzophenone tetracarboxylic amide or imide (BFBA or BFBI) suitable for autocalve fabrication was developed. The preferred process for the BMPM - BFBA composition consists of impregnation of fiber with the resin at 30% w/w solids concentration in dimethyl formamide (DMF) employing a drum winding technique. The graphite prepreg is staged at 389°K (240°F) for 16 hours to produce a material of ∿2% volatiles and 40% w/w resin content suitable for lay-up and cure. The prepreg then is cut to the desired length and width dimensions and several plies are stacked to effect a proper thickness. This prepreg configuration then is bagged employing Kapton and introduced into an autoclave. The lay-up is cured employing a process cycle of raising the temperature to 380°K (225°F) at the rate of 3°K/min (5°F/min) under vacuum bag pressure, holding at 380°K for 120 minutes then raising the temperature at the same rate to 439°K (330°F). After 30 minutes at 493°K, positive pressure of 0.7 MN/m^2 (100 psi) is applied and the temperature is increased to 472°K (390°F). The part is cured at 472°K for 2 hours.

The partially cured composite product of high mechanical integrity then is placed in an air-circulating oven and postcured employing a staged cycle consisting of raising the temperature to 589°K (600°F) at the rate of 3°K/min (5°F/min) and then holding at 589°K for 6 hours. The finished composite prepared by this total process possesses an excellent combination of properties [e.g., 2-3% voids, 868 MN/m^2 (124 Ksi) flexural strength and 52 MN/m^2 (8 Ksi) short beam shear strength]. An average of 90% of the mechanical strengths are retained initially on testing at 589°K (600°F). The composite products are suitable for long-term use in air at 491°K to 561°K (500°F to 550°F).

8.2 NEW BIS(BENZIL) COMPOSITIONS OF MATTER

A route to prepare a new general class of bis(benzil) monomers was reduced to practice. The experimental method used to prepare a specific member of this compound class, 1,4-bis(2-furylglyoxaloyl) benzene, is described in Appendix C. The furan terminated bis(benzils) subsequently were used to prepare crosslinked PPQ resins. The synthesis procedure used to prepare this monomer also is of interest because it does not include a selenium dioxide oxidation step.

8.3 A NOVEL METHOD FOR CROSSLINKING POLYPHENYLQUINOXALINE RESINS

It was experimentally determined that linear polyphenylquinoxaline (PPQ) resins can be crosslinked by employing a backbone monomer and a crosslinking agent of similar or identical structures to those used in the PDA polymer process. Specifically, a new PPQ linear polymer was prepared from 10% m/m 1,4-bis(2-furylglyoxaloyl) benzene, 40% m/m *p,p'*-oxydibenzyl and 50% m/m 3,3'-diaminobenzidine in a 1:1 (v/v) mixture of *m*-cresol/xylene. The linear polymer was crosslinked by dissolving it and 10% m/m BMPM in *m*-cresol at 298°K (75°F), then heating the solution for one hour at 473°K (200°F). During this treatment at 473°K, a solid product assumed to be crosslinked, precipitated from the solution. This product was isolated and shown to be insoluble in either hot *m*-cresol or concentrated sulfuric acid giving evidence that crosslinking indeed occurred.

This new crosslinking chemistry is thought to be of general applicability to PPQ's. It should constitute the highly sought-after method to eliminate the high temperature thermo-plasticity deficiency of existing PPQ resins and be of high practical utility for preparing useful, resin molded, reinforced composite and adhesive products from this polymer system.

8.4 QUINOXALINE-IMIDE COMPOSITIONS OF MATTER

Several new quinoxaline-imide resin compositions of matter were prepared employing the poly(Diels-Alder) (PDA) reaction. Specifically, polymers prepared by heating equal molar quantities of difurylquinoxaline (DFQ) with 1,3-dimaleimidobenzene (DMB) or bis(4-maleimidophenyl) methane (BMPM) at 497°K (450°F) under an applied pressure of 1.4 MN/m^2 (200 psi) for two to four hours, followed by postcure at 589°K (600°F) in nitrogen for four to eight hours yielded consolidated resin specimens of initial thermo-oxidative stability >589°K (600°F). Preliminary evidence was gained that composites of greater mechanical strengths than PDA derived homo-polyimides can be autoclave fabricated in a similar manner to the methodology described in 8.1.

APPENDIX A

The following experimental procedures are offered as representative methods to prepare 2-amino-5-norbornene structures and methyl substituted nadic anhydride compounds as well as their corresponding phthalimide and N-phenyl imide derivatives, respectively. The specific procedures given as representative are those employed to prepare 2-amino-5-norbornene (I), 2-phthalimido-5-norbornene (IX), 2-methylnadic anhydride (VI) and N-phenyl-2-methyl nadimide (XIV). Preparation and characterization of bis (4-nadimidophenyl) methane (XVII) is also described.

A.1 SYNTHESIS OF 2-AMINO-5-NORBORNENE (I)

The following procedures describe the Curtius reaction steps used to prepare compound I. The method of Parkham, et al was employed throughout (Reference 12).

A.1.1 Synthesis of 2-Carbomethoxy-5-norbornene

The Diels-Alder addition of cyclopentadiene to methyl acrylate proceeded smoothly and gave the desired product in reasonable yield. The experimental procedure employed is given below:

> A mixture of 258 g (3.0 moles) of methyl acrylate and 198 g (3 moles) freshly distilled cyclopentadiene were combined under a reflux condenser. After a short initiation period, the mixture heated autogenously and began to reflux necessitating cooling with a pan of ice water. After reflux ceased, the reaction mixture was distilled. Material boiling at 343-363°K (70-90°C) under reduced pressure (23 torr) was collected to yield 346 g (2.3 moles) or 76% of product; $n_d^{25°}$ 1.4729, literature $n_d^{25°}$ 1.4745 (Reference 12).

Verification of desired ester formation was performed by IR analysis. The endocyclic ester was converted to hydrazide by the procedure given below.

A.1.2 Preparation of the Hydrazide of 2-Carboxy-5-norbornene

The 2-carbomethoxy-5-norbornene obtained above was converted in quantitative yield to its corresponding hydrazide by the procedure given below:

> A mixture of 112 g (0.7 mole) 2-carbomethoxy-5-norbornene 70 ml hydrazine, 40 ml water, and 180 ml ethanol was refluxed for 24 hours, then volatile reactants were removed on a rotary evaporator. The resulting oil crystallized from water. The resulting solid was filtered, then dried in a vacuum oven to yield 112 g (0.7 mole) or 100% of product; m.p. 334°K-360°K; literature 333°K-357°K (Reference 12).

The wide melting range is due to the presence of endo and exo substitution. Formation of the desired product was confirmed by IR analysis. The hydrazide was subjected to a Curtius rearrangement reaction to yield the desired endocyclic amine by the method described below.

A.1.3 Preparation of 2-amino-5-norbornene (I)

The hydrazide obtained as described in Section 2.3.s was converted to 2-amino-5-norbornene (I) by the reactions described below:

> A quantity of 110 g (0.7 mole) of the hydrazide of 2-carboxy-5-norbornene was dissolved in 750 ml water containing 62 ml of concentrated hydrochloric acid. The solution was cooled to 273°K (0°C) and 350 ml cold carbon tetrachloride (CCl_4) was added. A solution of 50 g (0.7 mole) of sodium nitrite in 150 ml of water was cooled to 273°K (0°C) and added slowly with occasional stirring to the hydrazide hydrochloride. The CCl_4 layer containing the azide was separated from the aqueous layer and placed in a flask fitted with a stirrer and reflux condenser. Sixty-two ml hydrochloric acid in 220 ml water was added to the CCl_4 solution and the mixture was heated gently until nitrogen evolution signaled the decomposition of the azide. Heat was removed and the decomposition continued for two hours. The stirrer was arranged to mix the interface of the two phases, the reaction was brought to reflux, and heating and stirring were continued for 72 hours. The acidic aqueous solution was separated, rendered basic by addition of potassium hydroxide pellets, then extracted three times with ether. The extracts were dried over sodium sulfate, then the ether was evaporated to give 37.5 g (0.4 mole) of liquid amine product (49%).

Preparation of the endocyclic amine was confirmed by IR analysis. The spectrum of 2-amino-5-norbornene is shown in Figure A.1. The desired presence of primary amine is indicated by absorptions at 3360 cm^{-1}, 3280 cm^{-1} and 1590 cm^{-1}. The rearrangement was apparently complete due to the absence of any carbonyl absorptions in the region of 1700 cm^{-1} to 1800 cm^{-1}.

A.2 PREPARATION OF 2-PHTHALIMIDO-5-NORBORNENE (IX)

The amine structure I was directly converted to the corresponding phthalimide as described below. For further characterization of the imide, see Section A.3.

> In a round bottom flask equipped with a reflux condenser and a Dean-Stark trap, 40.8 g (0.37 mole) 2-amino-5-norbornene and 55.3 g (0.37 mole) phthalic anhydride were combined in toluene, and refluxed until the theoretical amount of water was collected. A solid product was isolated by cooling the reaction mixture. Recrystallization from ether (twice) yielded 26.6 g (30%) of imide; m.p. (DSC) = 368-370°K (95-97°C).

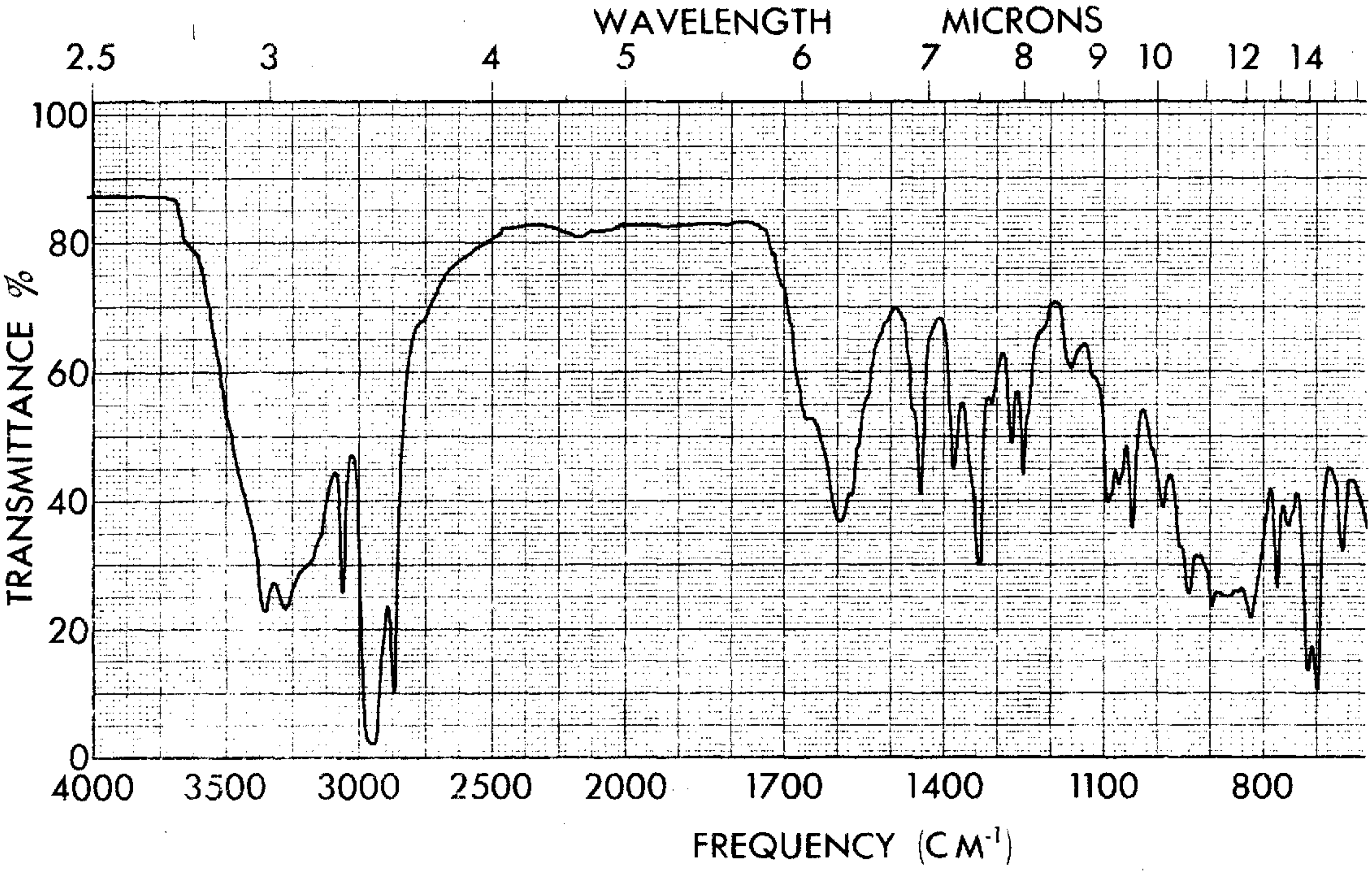


Figure A.1 Infrared Spectrum of 2-Amino-5-norbornene (I)-(Neat on NaCl)

A.3 CHARACTERIZATION OF MODEL IMIDES

The model imides were analyzed for structure by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.

A.3.1 Infrared Analysis (IR)

The IR spectra of representative model imide structures IX and XIV (representing the phthalimide and N-phenyl derivatives of amine compound I and anhydride compound VI) are shown in Figures A.2 and A.3 respectively. Similarities in the spectra include strong imide absorption bands near 1760 cm^{-1} and 1700 cm^{-1} for each and absorptions near 2900 cm^{-1}, 1300 - 1400 cm^{-1} and 710 - 720 cm^{-1}, tentatively assigned to elements of the norbornene endocyclic ring, since each was also present in the spectrum of precursors (see Figure A.1).

A.3.2 Nuclear Magnetic Resonance Analysis (NMR)

The success of converting endocyclic structures I to VIII to their imide derivatives, compounds IX to XVI, respectively, was confirmed by NMR. As expected, the complexity of proton absorption varies according to the presence of methyl substitution and, particularly, to the position of the substitution.

In general, the proton absorptions for phenyl protons in the phthalic or aniline derived portions of the molecule remained fairly constant at τ = 2.0 to 3.0. Otherwise, the remaining aliphatic methyl, methylene and methenyl or vinyl protons varied considerably according to the parent compound structure. The interpretations are made to "best fit" distinct proton absorptions.

The spectra of model imides IX and XIV are presented as Figures A.4 and A.5 respectively. Each spectrum has a structure of the specific model compound from which it was derived affixed in order to make the interpretations easier to follow.

- 2-Phthalimido-5-norbornene (Figure A.4)

  The aromatic protons band appear at τ = 2.23 and the two vinyl protons exhibit a triplet at τ = 3.77. The C-2 proton is shifted downfield to τ = 5.93 and the allylic protons appear as a broad singlet at τ = 7.00. The bridgehead protons are a very broad multiplet centered at τ = 7.63

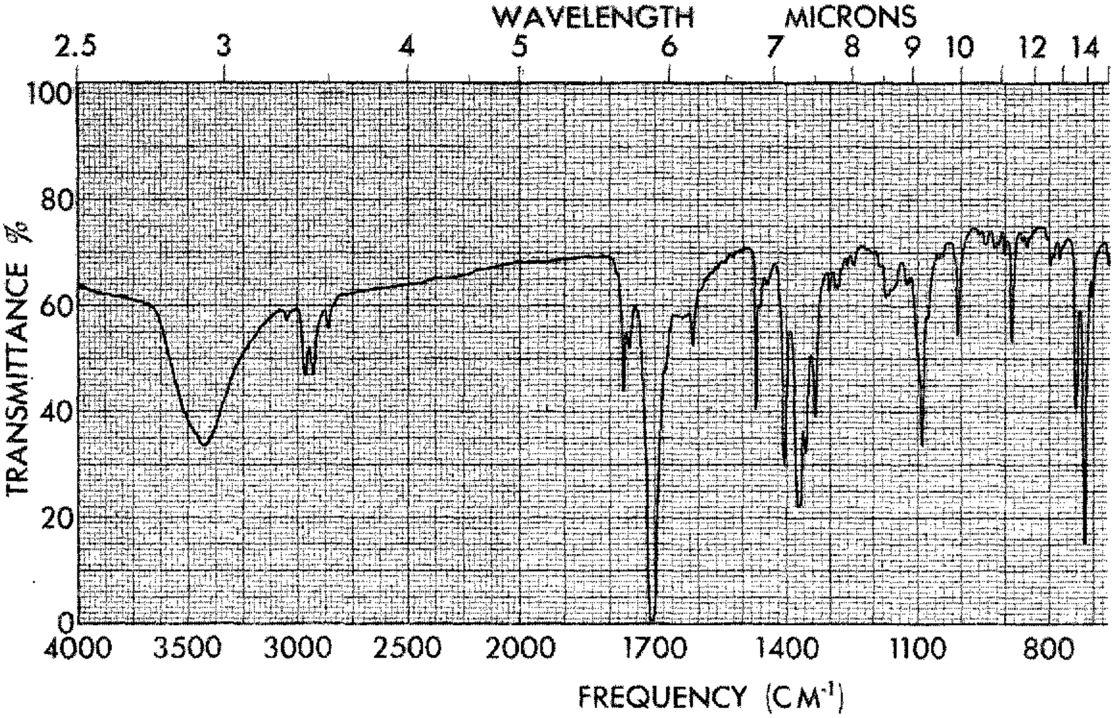


Figure A.2. Infrared Spectrum of 2-Phthalimido-5-norbornene (IX)-(KBr) Concentration: 3.3 mg/g KBr

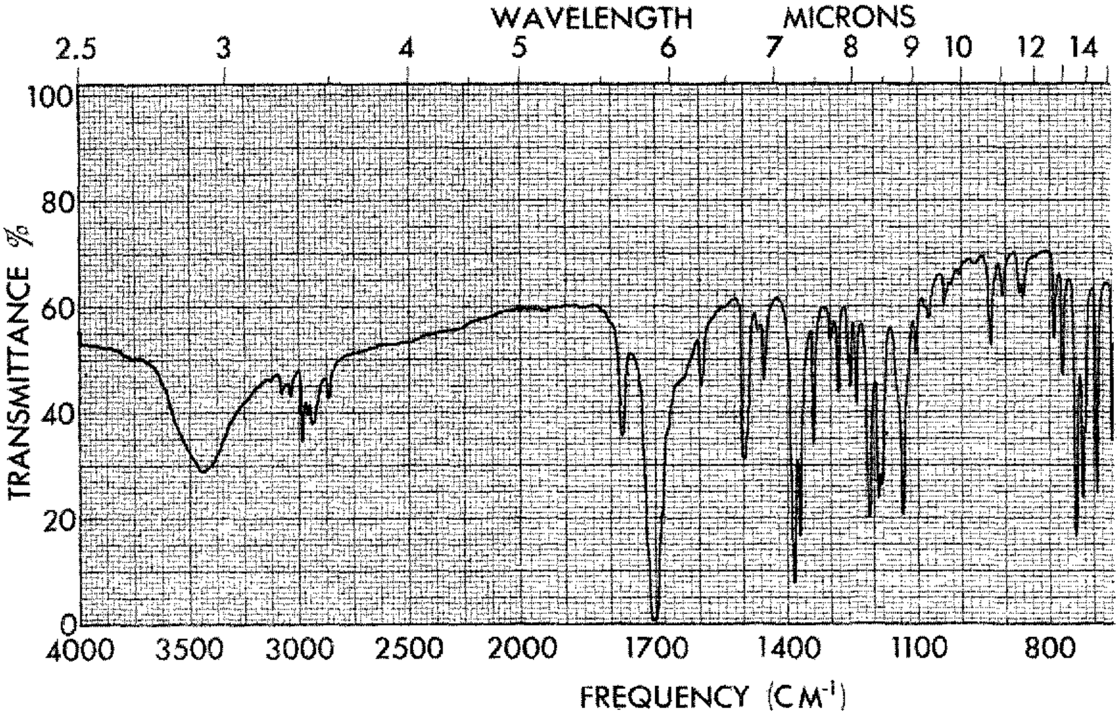


Figure A.3 Infrared Spectrum of N-Phenyl-2-methylnadimide (XIV)-(KBr) Concentration 3.3 mg/g KBr

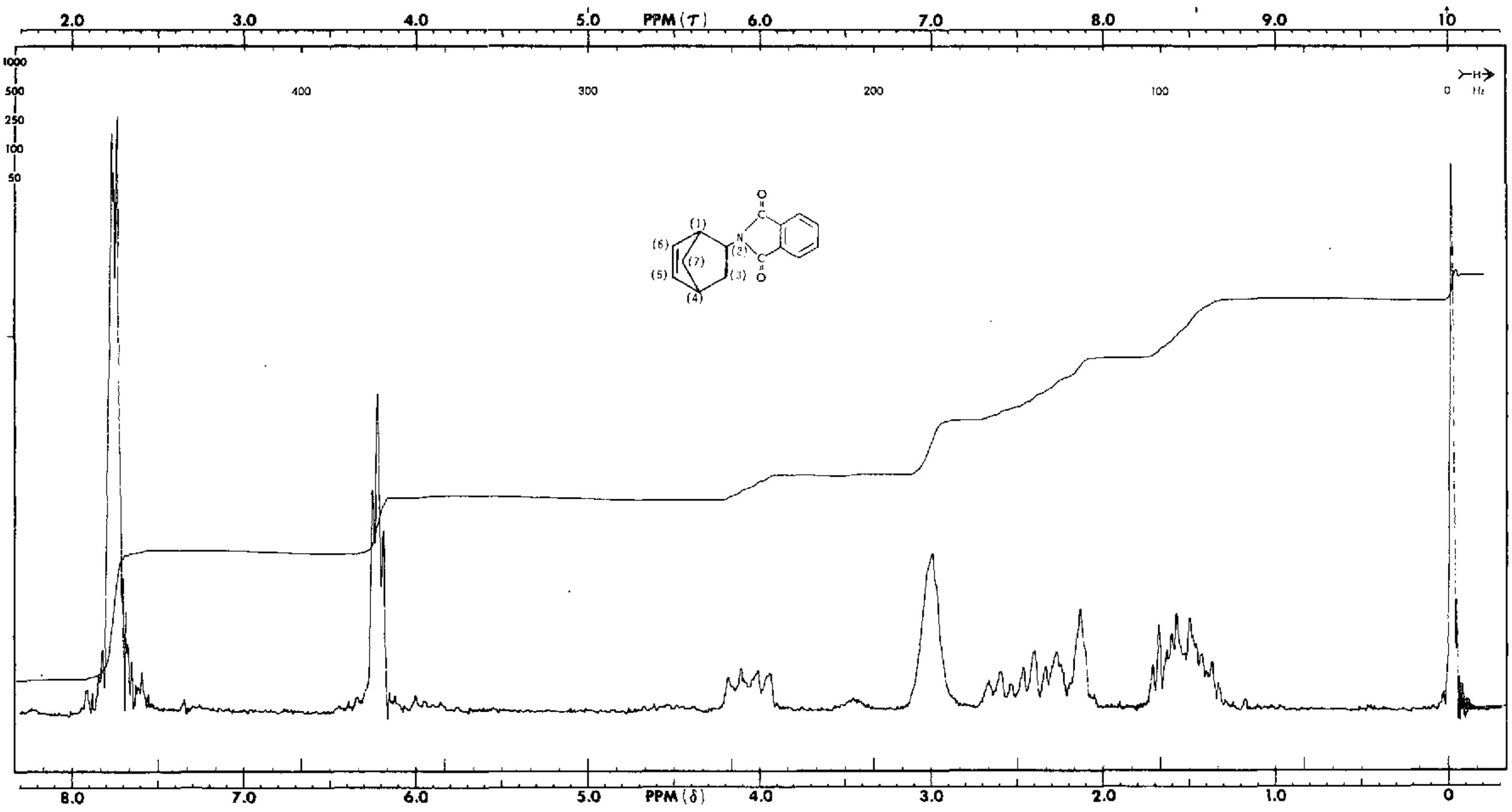


Figure A.4. Nuclear Magnetic Resonance Spectrum of 2-Phthalimido-5-norbornene (IX) Solvent: $CDCl_3$

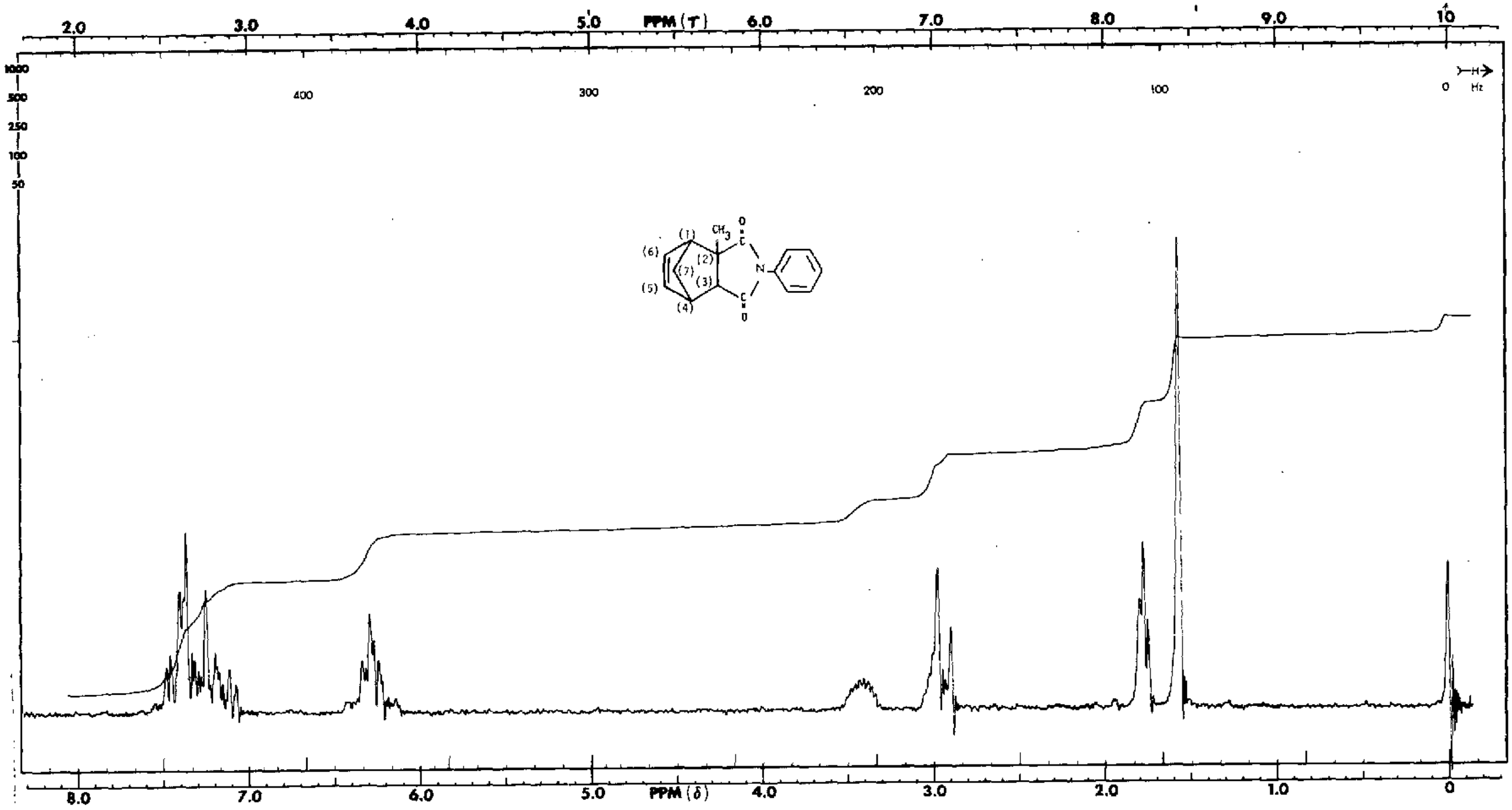


Figure A.5. Nuclear Magnetic Resonance Spectrum of N-Phenyl-2-methylnadimide (XIV)
Solvent: $CDCl_3$

while the multiplet for the C-3 protons is centered at τ = 8.47. The broadness of several proton absorptions in the model imide most probably stems from the presence of both exo and endo amino substitution.

- N-phenyl-2-methylnadimide (Figure A.5)

  The aromatic protons appear as a multiplet centered at τ = 2.72 and the vinyl proton band is also a multiplet at τ = 3.72. Further upfield the C-3 proton band is located at τ = 6.58 and is very broad. The allylic protons at C-1 and C-4 are a multiplet at τ = 7.03; the bridgehead protons also a multiplet at τ = 8.22, and the C-2 methyl is a sharp singlet at τ = 8.42.

The NMR spectra, although somewhat complex in nature, give strong evidence that the desired model imide structures had been prepared.

A.4 PREPARATION AND ANALYSIS OF BIS(NADIMIDE) MODEL COMPOUND

A.4.1 Synthesis of Bis(4-Nadimidophenyl) methane (BNPM-XVII)

A solution of 49.5 g (0.25 mole) of methylene dianiline in 50 ml of dimethyl formamide was added dropwise to a refluxing solution of 81 g (0.5 mole) of nadic anhydride in 300 ml of toluene. The mixture was refluxed for an additional 8 hours and then allowed to cool. The resulting precipitate was collected by filtration and the filter cake was washed with 200 ml of toluene. Recrystallization from toluene/dimethylformamide gave 85 g (70%) of bisimide; mp 527-530°K (254-257°C).

A.4.2 Characterization of Compound XVII

The BNPM model compound, so prepared, was analyzed to possess the correct structure by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The IR curve for XVII is shown in Figure A.6. This spectrum shows the desired imide bands to be present at 1710 cm^{-1} and 1770 cm^{-1} and the absence of undesired amide-acid bands in the region of 1630 cm^{-1}. A further fix on the correct structure was achieved by NMR analysis. The NMR spectrum is shown in Figure A.7. All proton absorption bands expected are present in the scan as follows:

- For MDA backbone; phenyl bands centered at 2.93τ; methylene at 6.03τ.

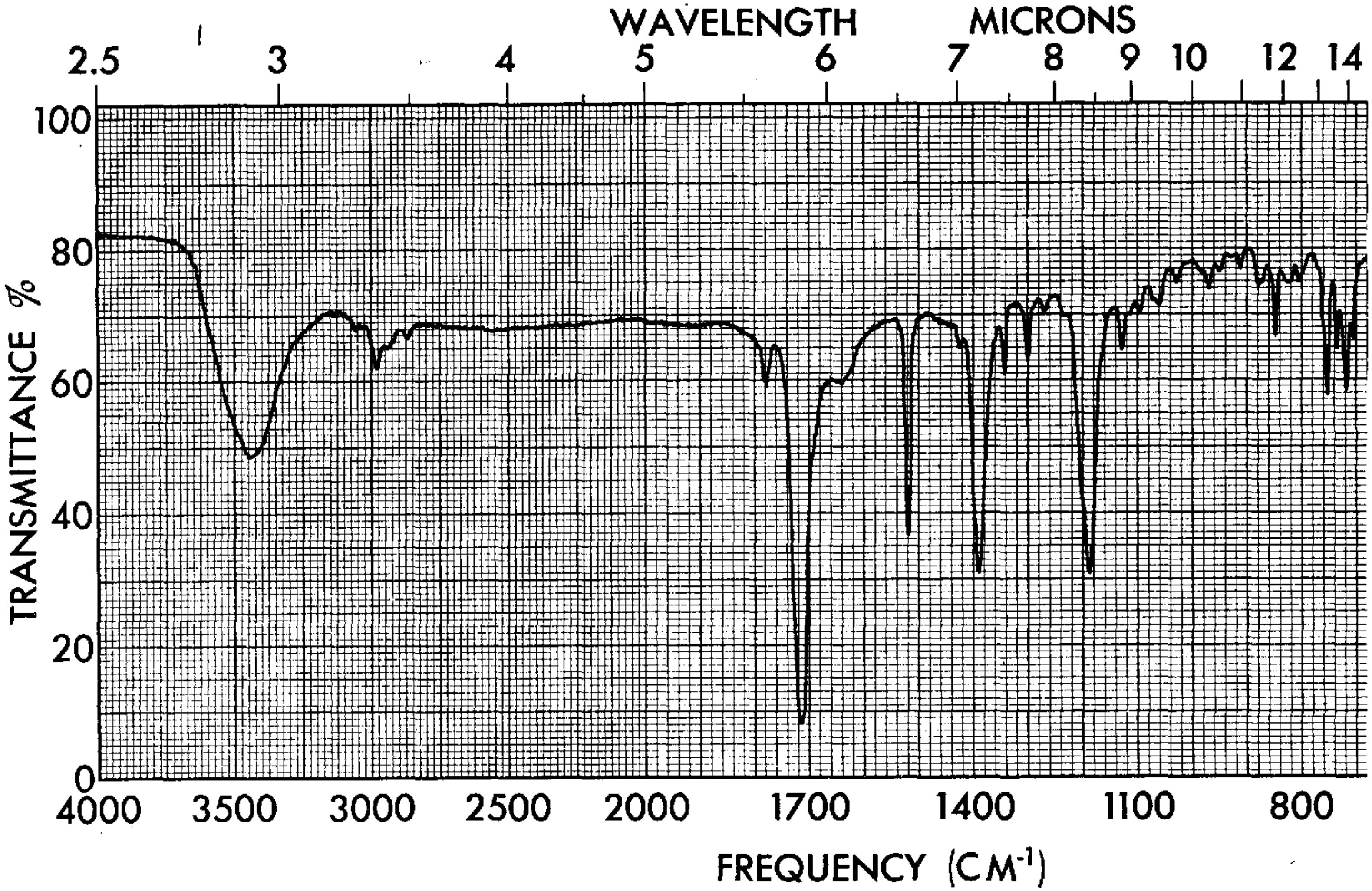
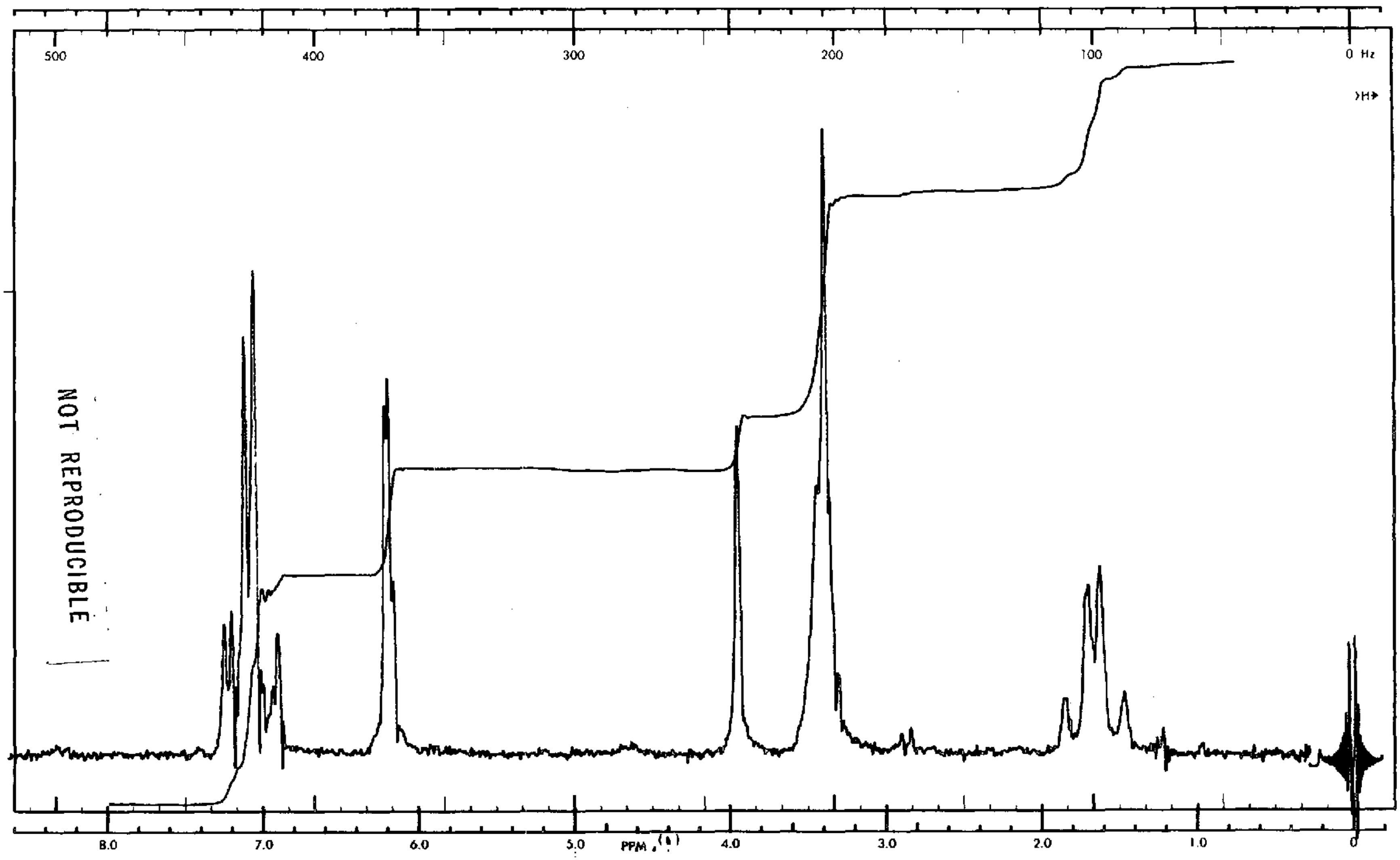


Figure A.6. Infrared Spectrum of Bis(4-nadimidophenyl) Methane (KBr)
Concentration: 3.1 mg/g KBr



NOT REPRODUCIBLE

Figure A.7. Nuclear Magnetic Resonance Spectrum of Bis(4-nadimidophenyl) methane
Solvent: DMSOd$_6$

- For NA entity: methylene bridge at 8.33τ; vinyl proton bands and methenyl proton bands at 6.60τ.

This material was subjected to key pyrolysis/postcure experiments (see Section 2.4.1).

APPENDIX B

The synthesis procedures used to prepare the compounds investigated in Task II are described below. Spectra employed to confirm desired structures are also presented. An example of a poly(Diels-Alder) reaction also is presented.

B.1 SYNTHESIS OF BIS(2-FURFURYL) PYROMELLITIMIDE (BFPI)

To a mixture of 87.2 g (0.4 moles) of pyromellitic dianhydride and 300 ml of dimethylformamide was added 77.6 g (0.8 moles) of furfurylamine dropwise over a 30 minute period. The mixture was stirred an additional 20 minutes and then 500 ml of xylene was added. The reactions mixture was heated to reflux and heating was continued for 16 hours during which time the water from the imidization reaction was collected in a Dean-Stark trap. The mixture was cooled to 273°K (0°C) and the resulting preciptate was collected by filtration. Recrystallization from acetone afforded 114 g (76%) of bisimide; mp 495-497°K (222-224°C). The infrared and nuclear magnetic resonance spectra are shown in Figure B.1 and Figure B.2, respectively.

B.2 SYNTHESIS OF BIS(4-MALEIMIDOPHENYL) METHANE (BMPM)

To a solution of 158 g (0.8 mole) of methylenedianiline in 480 ml of dimethyl formamide was added a solution of 157 g (1.6 moles) of maleic anhydride in 240 ml of dimethyl formamide at such a rate as to keep the temperatures below 343°K (70°C). After stirring the mixture for an additional 15 minutes, it was cooled to room temperature and 204 g (2 moles) of acetic anhydride followed by 16 g (0.2 moles) of sodium acetate was added. The resulting mixture was heated to 323°K (50°C) and maintained there for 3 hours. The crude product was precipitated by pouring the reaction mixture into 4000 ml portions of water. The precipitate was collected by filtration, washed twice with 4000 ml portions of water and dried. Crystallization from methanol afforded 203 g (71%) of bisimide, mp 429-432°K (156-159°C). The infrared and nuclear magnetic resonance spectra are presented in Figure B.3 and Figure B.4, respectively.

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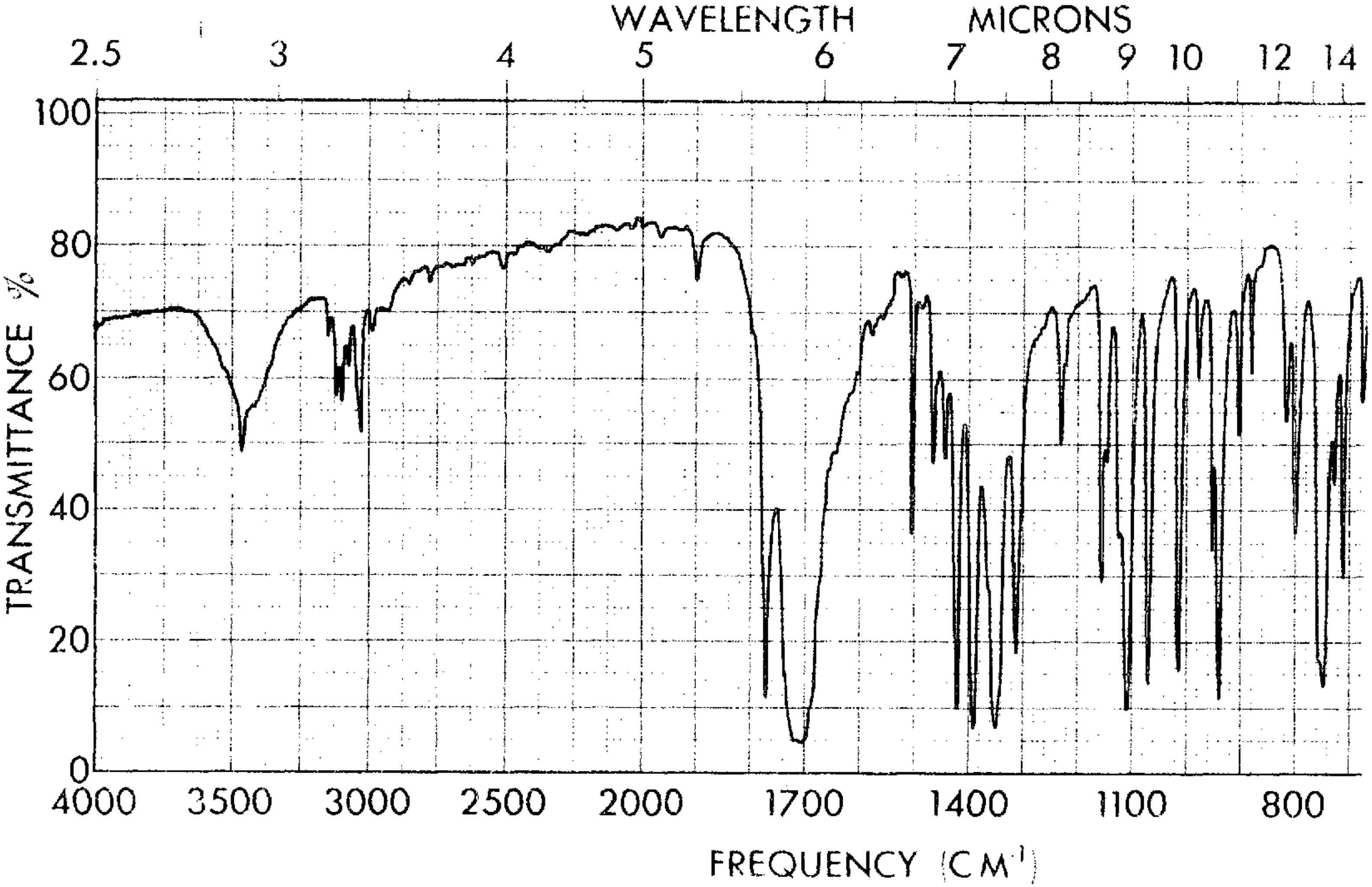
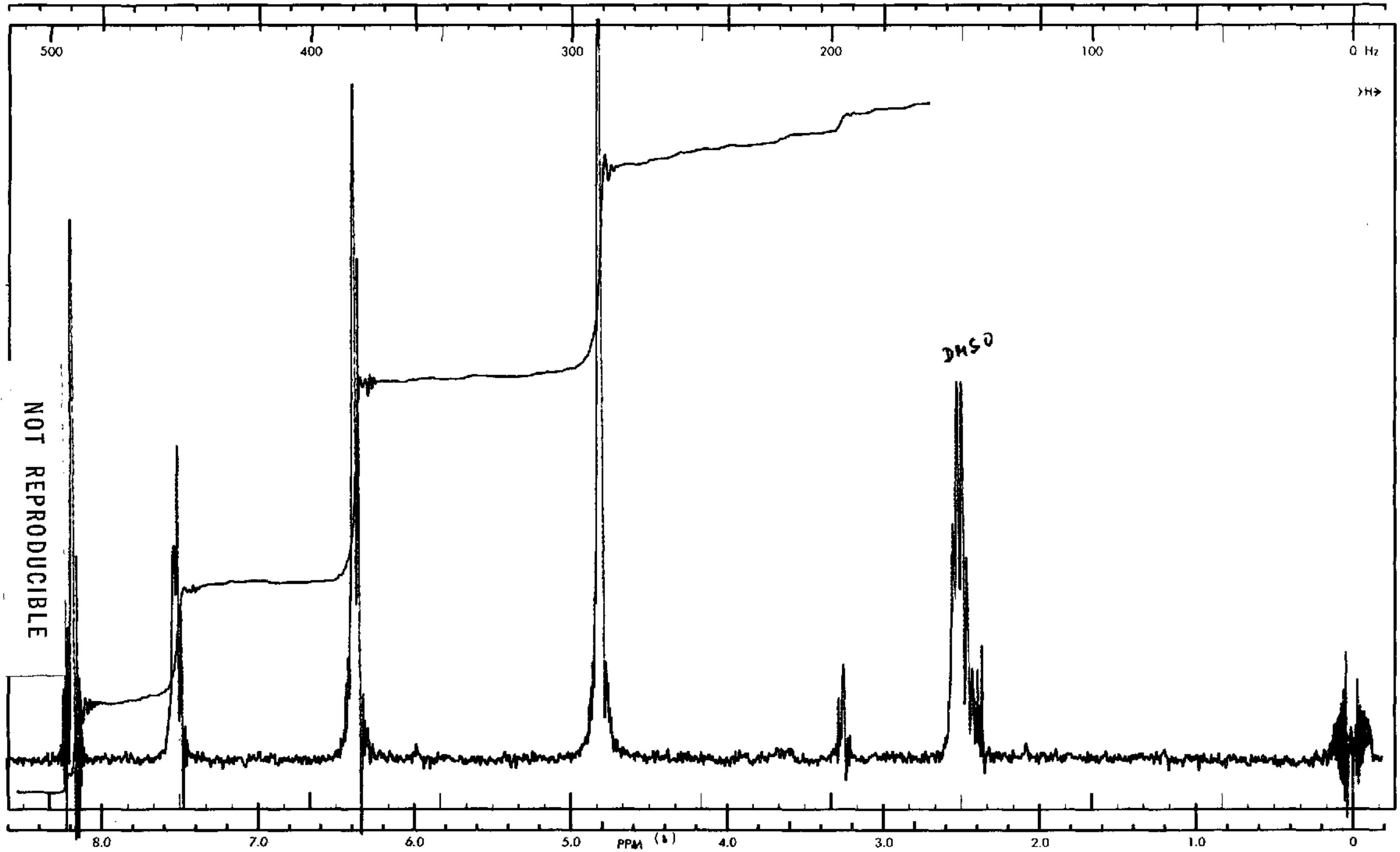


Figure B.1. Infrared Spectrum of Bis(4-furfuryl) pyromellitimide (KBr)
Concentration: 3.0 mg/g KBr



NOT REPRODUCIBLE

Figure B.2. Nuclear Magnetic Resonance
Spectrum of Bis(furfuryl) pyromellitimide
Solvent: DMSOd_6

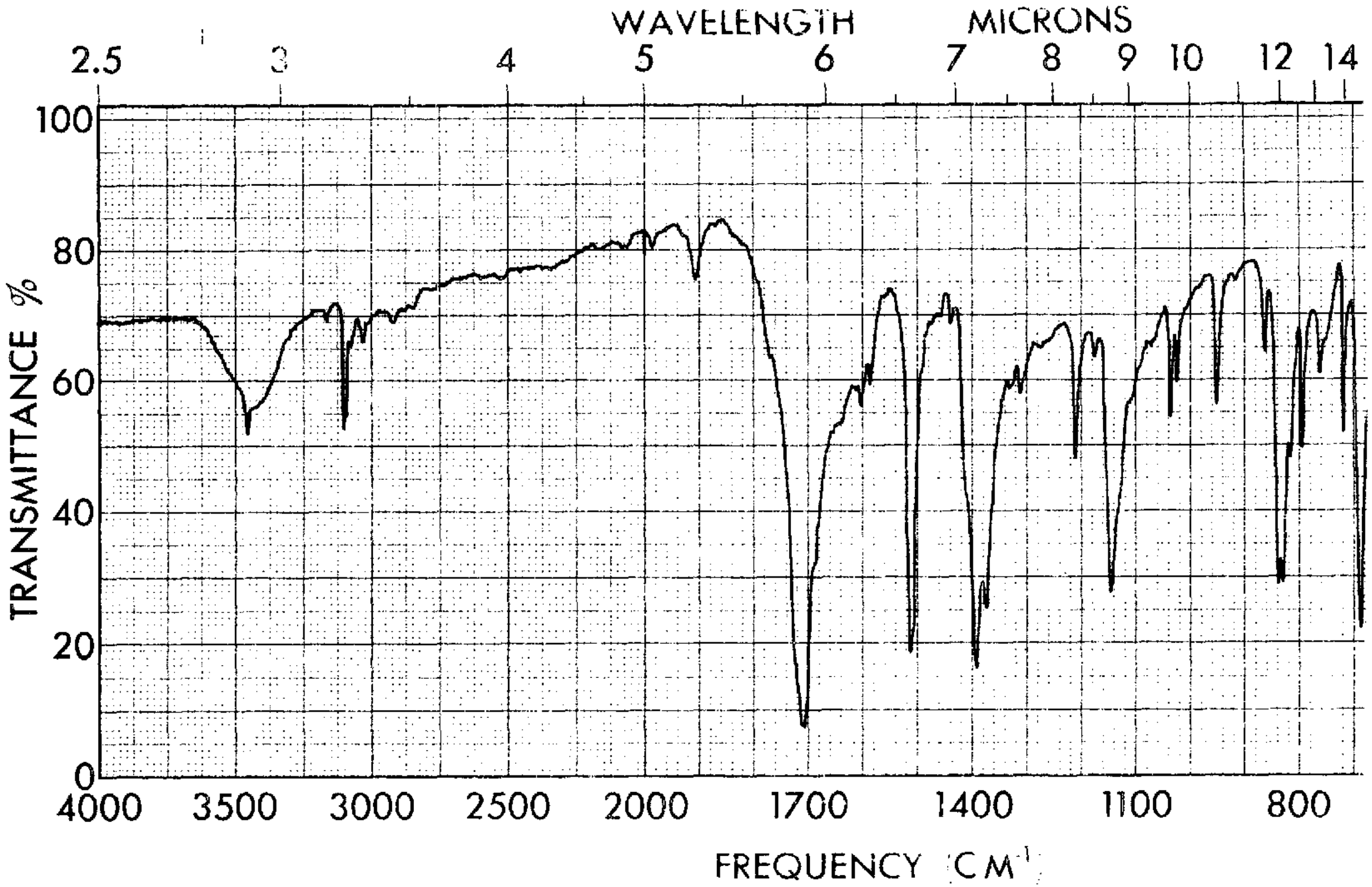


Figure B.3. Infrared Spectrum of Bis(4-maleimidophenyl) methane (KBr)
Concentration: 3.1 mg/g (KBr)

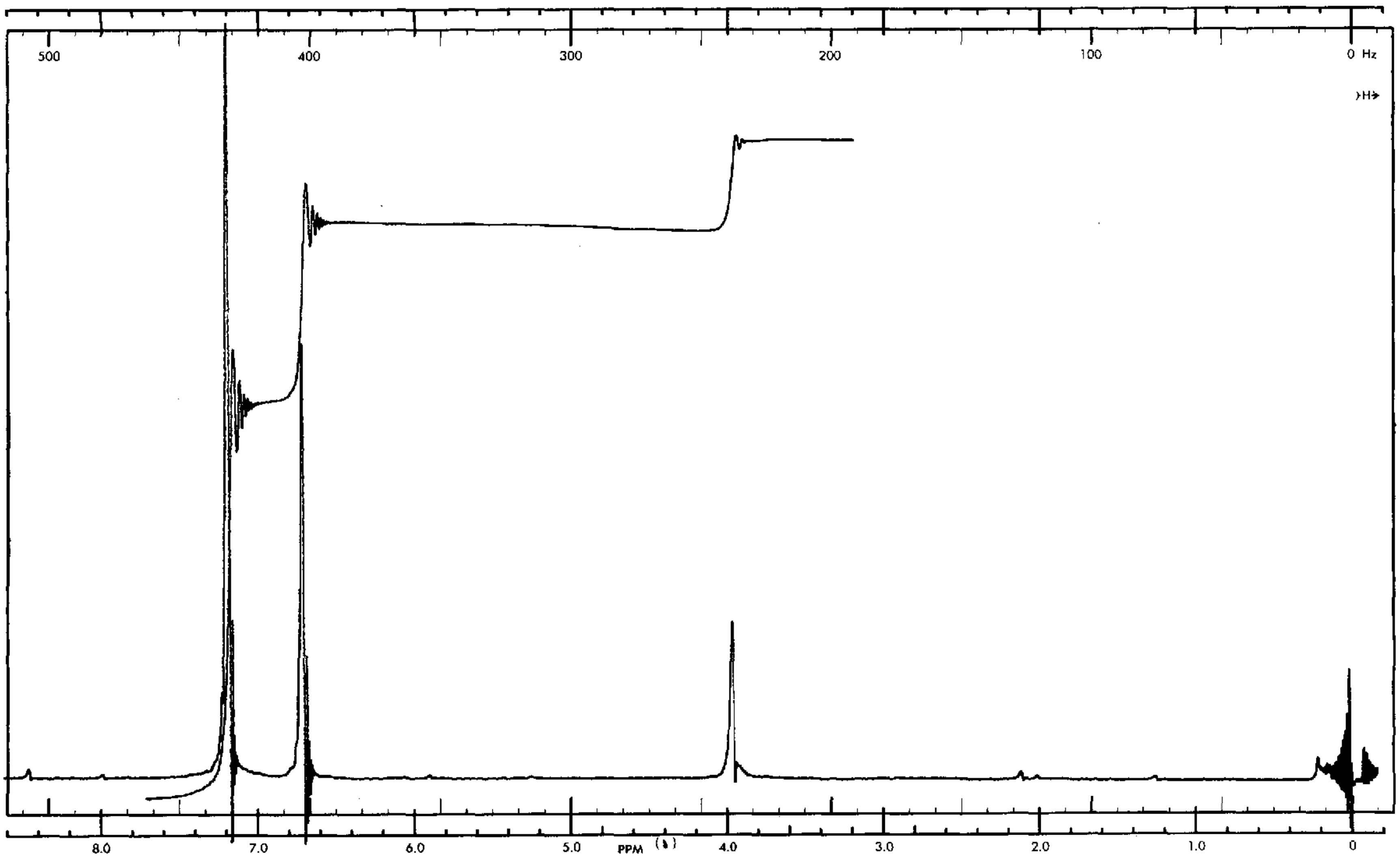


Figure B.4. Nuclear Magnetic Resonance Spectrum of Bis(4-maleimidophenyl) Methane
Solvent: DMSOd_6

B.3 SYNTHESIS OF BIS(2-FURFURYL) BENZOPHENONE TETRACARBOXYLIC IMIDE (BFBI)

To a solution of 258 g (0.8 mole) of BTDA in 600 ml DMF was slowly added 150 g (1.6 mole) of furfurylamine. The mixture was stirred an additional twenty minutes after the amine was added and then 1000 ml of xylene was added. The mixture was refluxed for 12 hours during which time the water of imidization was removed with a Dean-Stark trap. The reaction mixture was allowed to cool and the resulting precipitate was collected by filtration. Recrystallization of the filter cake from xylene afforded 261 g (68%) of bisimide; mp 506-508°K (233-235°C). The infrared and nuclear magnetic resonance spectra are given in Figure B.5 and Figure B.6, respectively.

B.4 SYNTHESIS OF THE MONOMETHYL ESTER OF NADIC ACID (NE)

A mixture of 492 g (3.0 mole) of nadic anhydride and 240 g (7.5 mole) of anhydrous methanol was refluxed for 8 hours. The solution was then cooled and the resulting precipitate was collected by filtration. The filter cake was recrystallized from a petroleum ether/benzene mixture to afford 485 g (82%) of ester; mp 372-374°K.

B.5 SYNTHESIS OF THE DIMETHYL ESTER OF BENZOPHENONE TETRACARBOXYLIC ACID (BTDE)

A mixture of 1288 g (4.0 mole) and 2000 g (62.5 mole) of anhydrous methanol was refluxed for 7 hours. Methanol was removed from the resulting solution on a roto evaporator until a thick slurry was obtained. The slurry was then taken to dryness in a vacuum oven to give 1420 g (92%) of diester. The diester was used without further purification.

B.6 PYROLYSIS OF BIS(2-FURFURYL) BENZOPHENONE TETRACARBOXYLIC IMIDE (BFBI) AND BIS(4-MALEIMIDOPHENYL) METHANE (BMPM)

The procedure described below was used to polymerize various PDA resins and is given as an example of the general procedure used in screening potential resins in Task II studies.

A mixture of 2.40 g (0.005 mole) of BFBI and 1.79 g (0.005 mole) of BMPM was placed in the pyrolysis tube and inserted into the pyrolysis apparatus (see Figure 1). The mixture then was heated at 477°K (400°F) for four hours under 1.4 MN/m^2 (200 psi) pressure. The residue obtained from

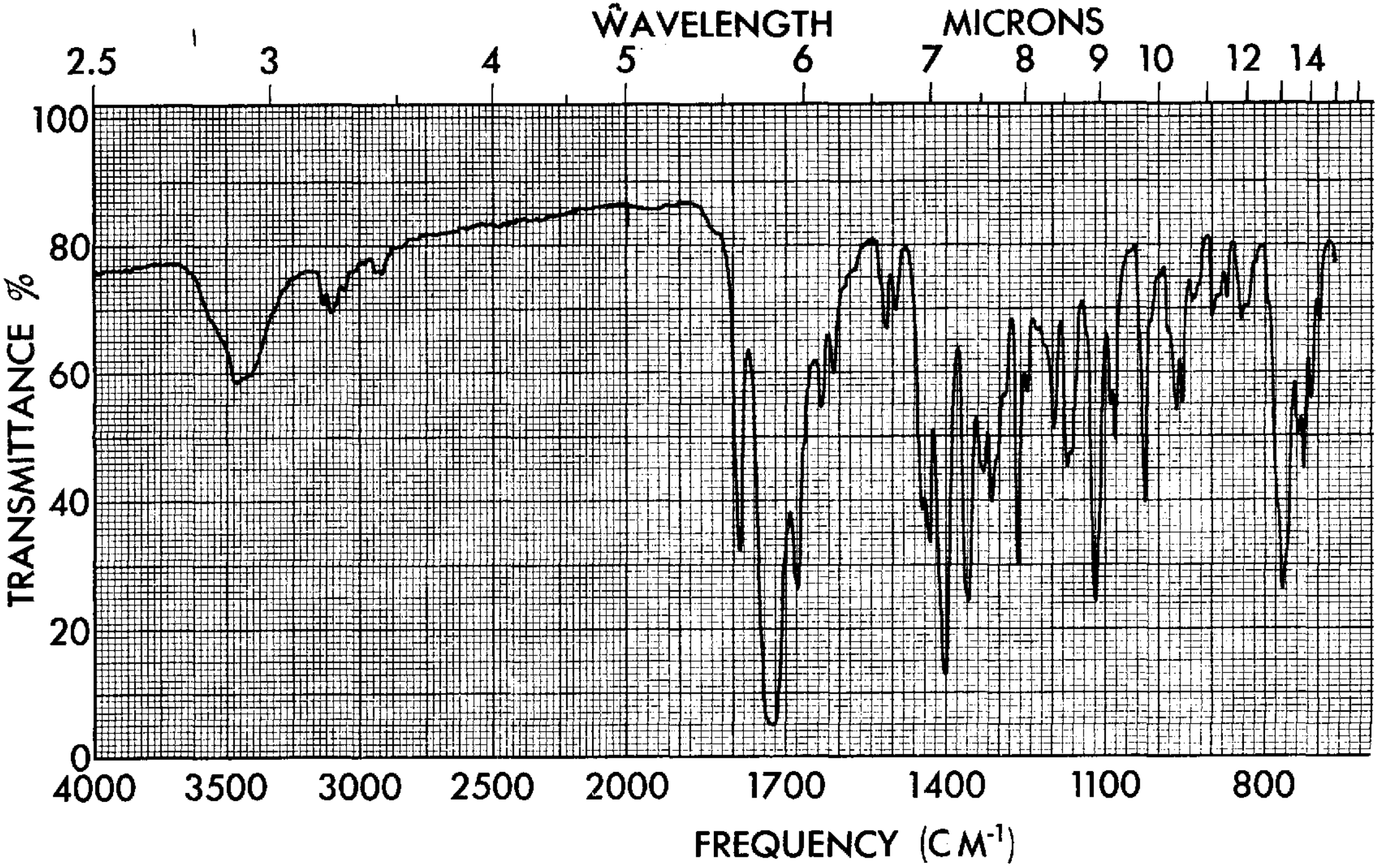


Figure B.5. Infrared Spectrum of Bis(2-furfuryl) Benzophenone Tetracarboxylic Imide
Concentration: 3.0 mg/g KBr

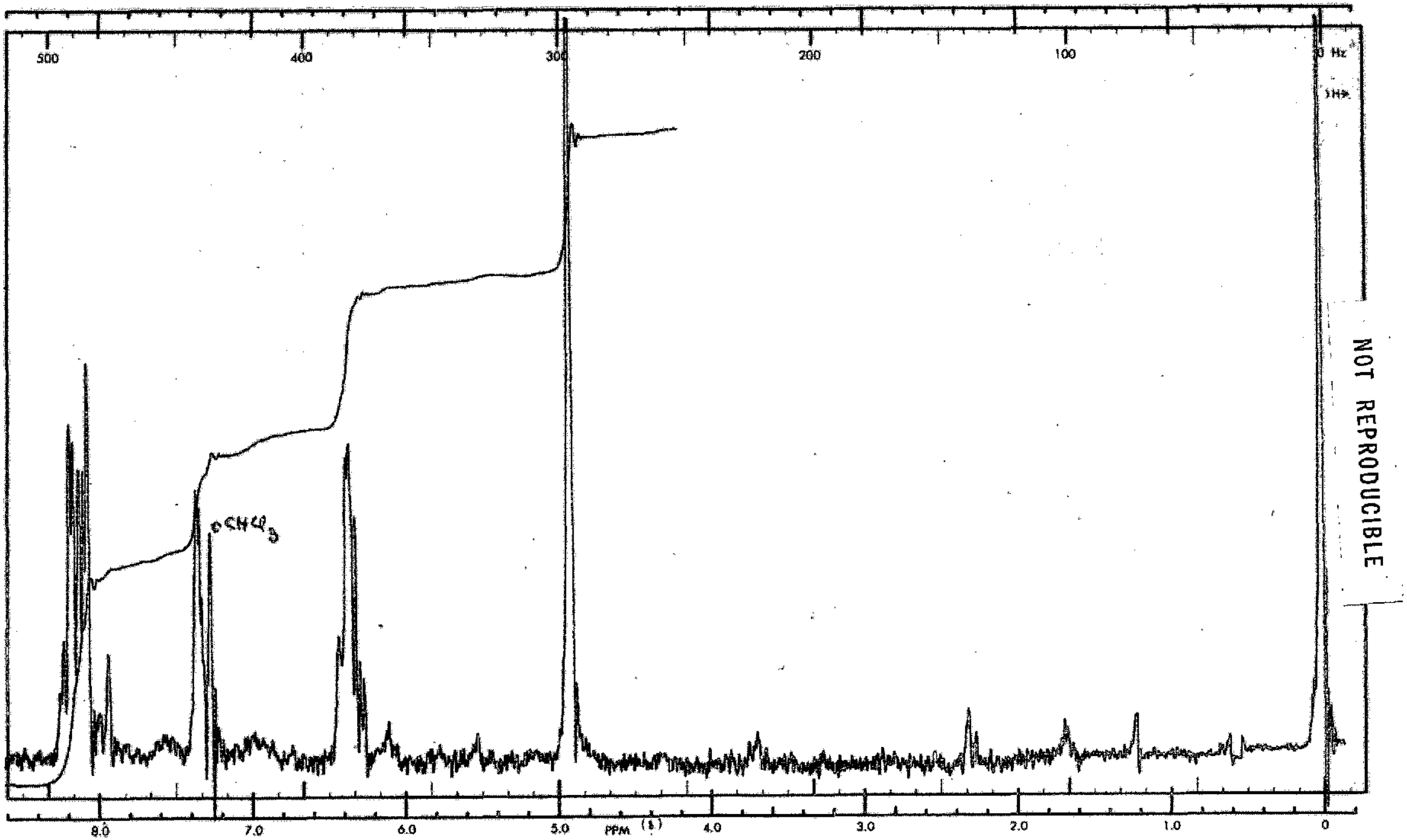


Figure B.6. Nuclear Magnetic Resonance Spectrum of Bis(2-furfuryl) Benzophenone Tetracarboxylic Imide
Solvent: $CDCl_3$

this experimentation was a well consolidated plug indicating melt polymerization had occurred. The solid plug was powdered and then postcured employing a 4 hour linear heat-up rate from 477°K to 589°K, followed by a 2 hour isothermal cycle at 589°K. Both the cured and postcured resin samples were subjected to thermogravimetric and infrared analyses. The infrared spectra for the cured and postcured samples are shown in Figure B.7 and Figure B.8, respectively.

B.7 PREPARATION OF PDA LAMINATING VARNISH

The general procedure employed to prepare the PDA laminating varnish is described below.

To a 1-ℓ. round bottomed flask were added 300 g of dimethylformamide and 64.40 g (0.2 mole) of BTDA. The slurry was stirred under a nitrogen atmosphere for 10 minutes and then the mixture was cooled to 278°K with an ice bath. To the cooled mixture was added 38.8 g (0.4 mole) of furfurylamine at such a rate so that the temperature was maintained below 293°K. After the addition was completed, the cooling bath was removed and the resulting solution was stirred for 1 hour. To the amic acid solution were added 21.7 g (0.2 mole) of BMPM and 108 g of DMF. The mixture was stirred at room temperature until a homogeneous solution was obtained. The varnish was carefully bottled and stored under nitrogen prior to use.

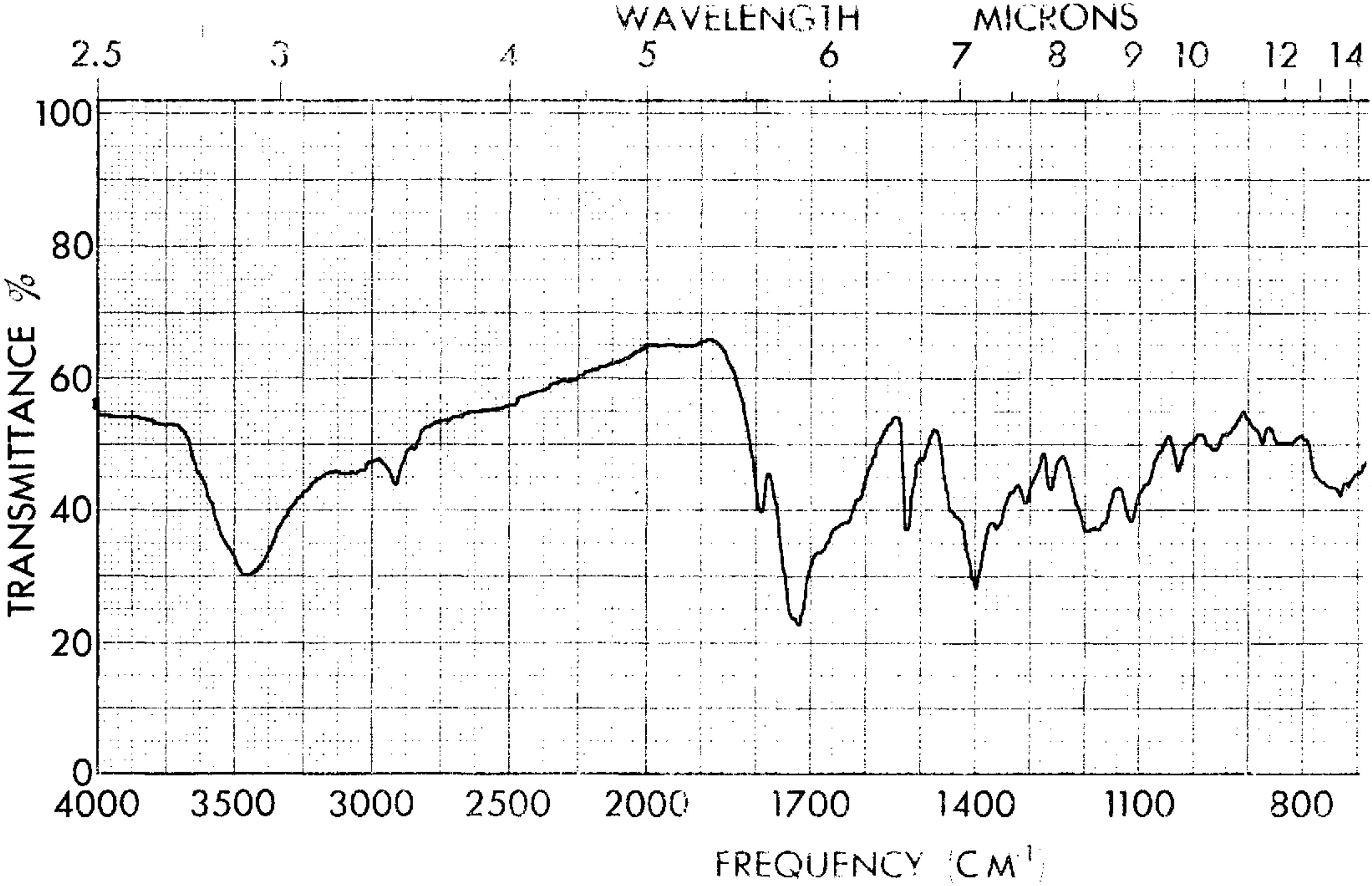


Figure B.7. Infrared Spectrum of BFBI/BMPM Mixture Cured at 477°K for 2 Hours (KBr)
Concentration: 3.2 mg/g KBr

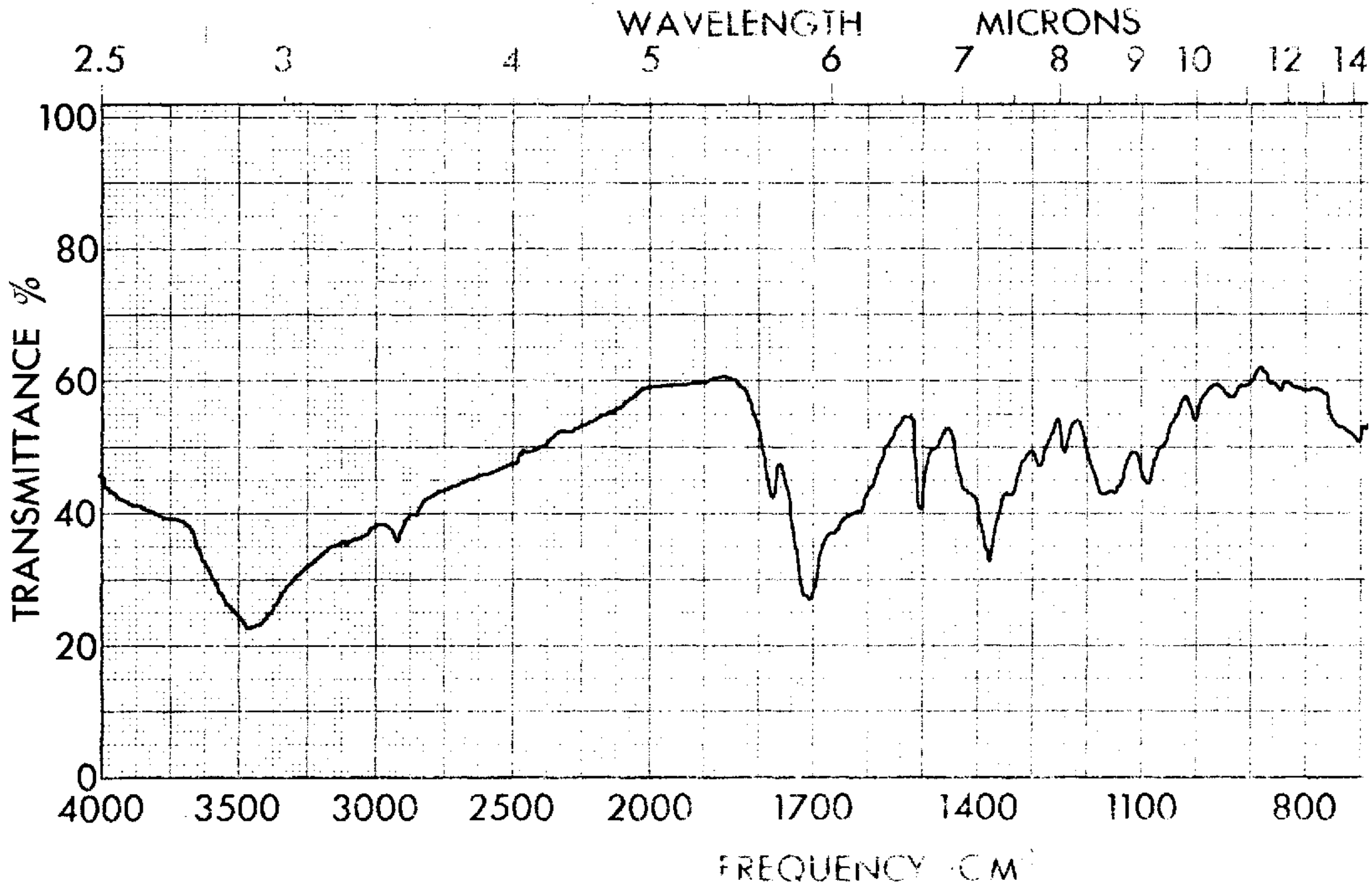


Figure B.8. Infrared Spectrum of BFBI/BMPM Mixture Cured at 477°K
and Postcured at 589°K (KBr)
Concentration: 3.0 mg/g KBr

APPENDIX C

The experimental procedures used to prepare 2,3-di-α-furylquinoxaline and its precursors are presented below. The routes employed to prepare a linear polyphenylquinoxaline and crosslink the polymer are also described. These materials were employed in Task IV and are discussed in Section 5.1.

C.1 PREPARATION OF FUROIN

To a mixture of 8000 ml of water, 1500 ml of ethanol and 2000 g (20.8 moles) of furfural heated to near reflux was added a solution of 100 g (1.54 moles) of potassium cyanide in 600 ml of water. Shortly after the addition was completed the reaction mixture began to reflux and refluxing was continued for 20 minutes. After the refluxing had ceased, the mixture was heated for an additional 10 minutes. The solution was allowed to cool, made acidic with acetic acid and cooled overnight in a refrigerator. The resulting crude furoin was collected by filtration and washed successively with cold methanol and with ether. The brown solid was recrystallized from methanol (charcoal) to give 712 g (35%) of furoin as light orange crystals.

C.2 PREPARATION OF FURIL

A well stirred mixture of 625 g (2.50 mole) of cupric sulfate pentahydrate in 270 ml of water and 630 ml of pyridine was heated until a solution was obtained. To this solution was added 220 g (1.25 moles) of furoin. The mixture was refluxed for 2 hours, cooled, and added to 4 l. of water. The tan precipitate was collected by filtration, washed well with water, and then recrystallized from methanol (charcoal) to give 155 g (71%) of furil as long yellow needles; mp. 435-437°K (162-164°C), lit. mp. 437-439°K (Reference 12).

C.3 PREPARATION OF 2,3-DI-α-FURYLQUINOXALINE (DFQ)

To a solution of 76 g (0.4 mole) of furil in 700 ml of acetic acid under a nitrogen atmosphere was added 43.3 g (0.4 mole) of *o*-phenylenediamine. The mixture was refluxed for 3 hours, allowed to cool and slowly added to 6 l. of water. The resulting precipitate was collected by filtration and washed well with water. Recrystallization of the tan solid from ethanol (charcoal) gave 93 g (89%) of substituted quinoxaline. The infrared spectrum of this compound is shown in Figure C.1.

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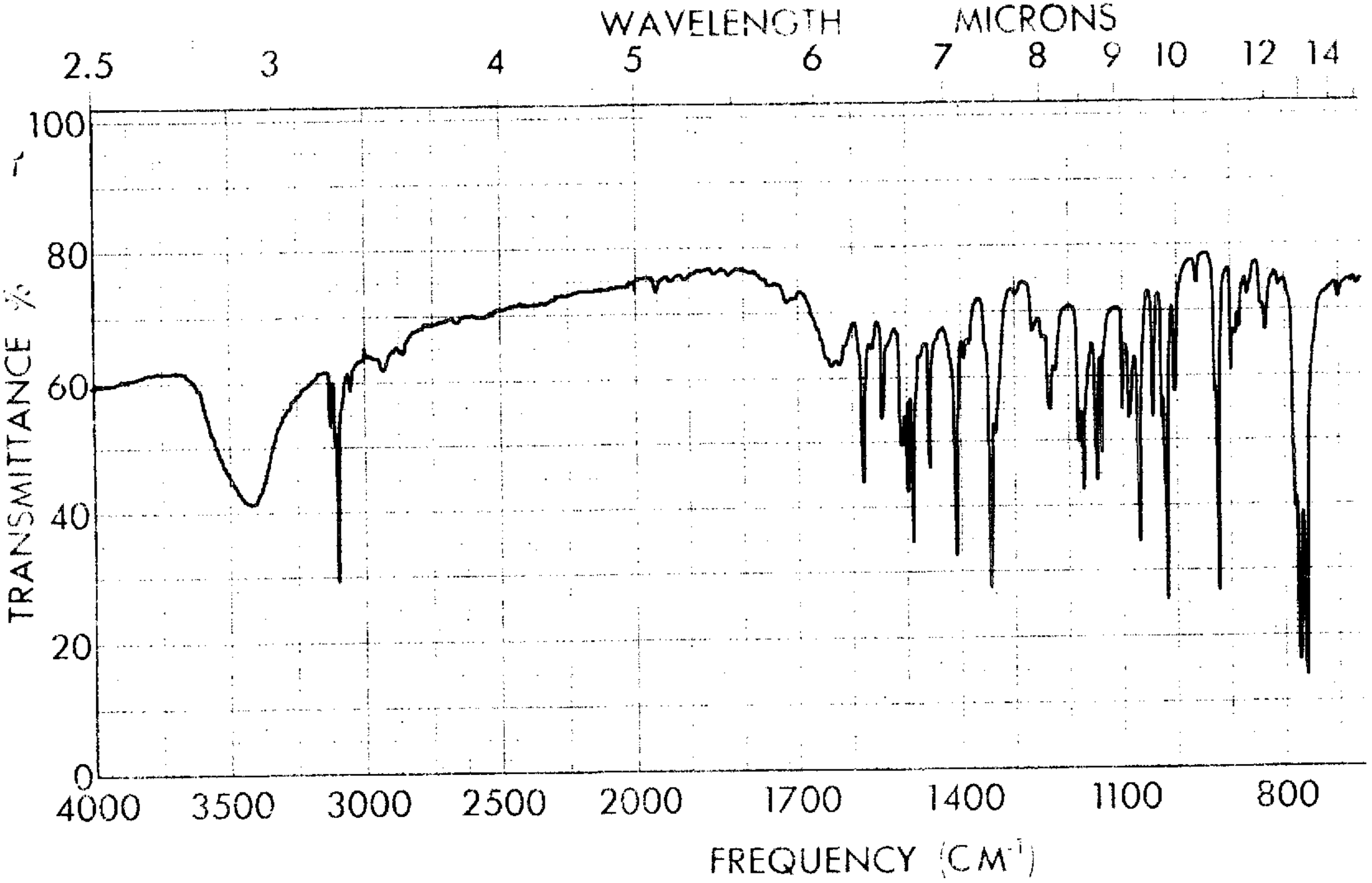

Figure C.1. Infrared Spectrum of 2,3-Di-α-furylquinoxaline (DFQ)
Concentration: 3.1 mg/g KBr

C.4 PREPARATION OF 1,4-BIS(2-FURYLGLYOXALOYL) BENZENE

To a mixture of 5.36 g (0.04 mole) of terephthaldehyde, 7.68 g (0.08 mole) of freshly distilled furfural and 80 ml of ethanol was added a solution of 10.0 g (0.152 mole) of potassium cyanide in 40 ml of water. An exotherm was observed during the cyanide addition and a solid was observed after 20 ml of the solution had been added. The reaction mixture was refluxed for two hours and then cooled to room temperature. The precipitate was collected by filtration and washed with ethanol. Recrystallized from a DMF/ethanol mixture gave 4.4 g (34%) of bis(hydroxyketone) materials; mp 503-506°K.

A well stirred mixture of 11.9 g (0.048 mole) of cupric sulfate pentahydrate in 6.0 ml of water and 14.0 ml of pyridine was heated until a solution was obtained. To this solution was added 4.0 g (0.012 mole) of bis(hydroxyketone) material prepared above and the mixture was refluxed for five hours. After twenty minutes of refluxing the initially blue solution had changed to green. The mixture was cooled to room temperature and then added to 500 ml of water. The precipitate was collected by filtration, washed well with water and recrystallized from ethanol (charcoal). The fine yellow needles were collected by filtration and air dried to give 3.1 g (78%) of 1,4-bis(2-furylglyoxaloyl) benzene; mp 467-469°K.

C.5 PREPARATION OF FURAN CONTAINING PPQ

To a slurry of 0.643g (3 mmole of diaminobenzidine in 7 g of a 1:1 mixture of xylene and *m*-cresol was added a mixture of 1.172 g (2.7 mmole) of oxybisbenzil and 0.097 g (0.3 mmole) of 1,4-bis(2-furylglyoxloyl) benzene during a two minute period. An additional 3 g of solvent mixture was added and the reaction mixture was stirred under nitrogen for 18 hours. The viscous solution was then slowly added to 500 ml of methanol in a blender. The fiberous yellow solid was collected by filtration, boiled twice with methanol and dried *in vacuo* at 473°K to give 1.65 g of polymer.

C.6 CROSSLINKING REACTION

A mixture of 0.557 g of PPQ (prepared above) and 0.036 g of bis(4-maleimidophenyl) methane in 5.5 g of *m*-cresol was heated to 477°K. In 1 hour a gel was obtained. The solvent was removed from the polymer at reduced pressure and the polymer so isolated was placed in sulfuric acid to assess if crosslink formation occurred. The polymer was observed to swell in the acid but it was not soluble.

APPENDIX D

PROCESS FOR AUTOCLAVE PREPARATION OF BFBI/BMPM-HMS COMPOSITES

Hercules HMS high modulus graphite fiber tows were impregnated with BFBI/BMPM amide-acid resin varnish (30% w/w in DMF) and collimated by drum winding at 35-36 tows/meter. The graphite fiber tows were impregnated in a resin bath and then wound onto a drum. Resin content level of the prepreg was maintained by controlling the resin viscosity (i.e. resin dilution). Characterization of the tape consisted of volatile matter and resin solids determination by solvent extraction using DMF as the solvent (see Appendix E for procedure). Tape was cut into 20.3 cm by 25.4 cm pieces and B-staged 16 hours at 336°K (145°F), 1 hour at 390°K (225°F) and 1 hour at 394°K (250°F). These 20.3 cm by 25.4 cm plies of graphite prepreg tape were stacked and vacuum bagged using conventional materials and techniques. The cure cycle was as follows:

1. 2 hours at 390°K (225°F) plus 20 minutes at 444°K (340°F) under vacuum bag pressure.
2. Apply 0.7 MN/m^2 (100 psi) positive pressure and raise the temperature to 472°K (390°F).
3. Cure for 2 hours at 472°K (390°F).

The vacuum bag assembly was cooled under vacuum bag pressure to room temperature and then the graphite composite was removed and postcured in an air circulating oven as follows:

1. 30 minutes at 481°K (400°F)
2. 1 hour at 505°K (450°F)
3. 1 hour at 533°K (500°F)
4. 1 hour at 559°K (550°F) and
5. 4 hours at 589°K (600°F)

APPENDIX E

TEST PROCEDURES FOR CHARACTERIZATION OF PREPREG AND COMPOSITES

E.1 RESIN CONTENT BY SOXHLET EXTRACTION

Samples of the graphite tape were weighed in a tared soxhlet extraction thimble and then placed in the soxhlet extraction apparatus. The solvent then was heated to a refluxing condition and remained refluxing until the solvent surrounding the thimble was clear. After removing the thimble from the extraction apparatus the thimble was oven dried to constant weight and reweighed. Wet and dry resin contents then were calculated as follows:

$$\text{Wet Resin Content - } W_{W.R.} = \frac{W_2}{W_1}\ (100)$$

$$\text{Dry Resin Content - } W_{D.R.} = \frac{W_2 - (W_2)V}{W_3 + [W_2 - (W_2)V]}$$

Where:

$W_{W.R.}$ = Weight content of wet resin solids, %

W_1 = Weight content of original sample

W_2 = Weight content of extract

$W_{D.R.}$ = Weight content of dry resin solids, %

V = Volatile matter content of graphite tape

W_3 = Weight content of graphite.

E.2 RESIN CONTENT BY ACID DIGESTION

The resin was digested from the cured sample 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 firstly in distilled water and then in acetone, after which the filaments were dried for 15 minutes in a 450°K 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

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

E.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 590°K for 30 minutes.

E.4 DENSITY OF COMPOSITES

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

E.5 COMPOSITE FIBER VOLUME

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

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

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 HMS fiber is 1.90 g/cm^3 and of the cured P10P polyimide resin is 1.30 g/cm^3.

E.6 COMPOSITE VOID CONTENT

Void contents of the composites were calculated using the formula:

$$V_v = 100 - D_c \frac{W_r}{D_r} + \frac{W_f}{D_f}$$

Where:

V_v = Volume of voids, % v/v

D_c = Measured density of composite, g/cm^3

D_r = Density of resin, g/cm^3

D_f = Desnity of fiber, g/cm^3

W_r = Weight content of resin, percent

W_f = Weight content of fiber, percent

E.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, 10-cm x 10-cm square) after removal of the resin flash.

Flow properties were calculated:

$$F_w = \frac{W_1 - W_3}{W_1} \quad (100)$$

and

$$F_d = \frac{W_2 - W_3}{W_2} \quad (100)$$

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

E.8 SHEAR STRENGTH OF COMPOSITES

The cured composites were machined into short beam shear specimens 0.63-cm wide x 1.78-cm long and tested in flexure at a mid-span loading point using a 4:1 span to depth ratio. Loading rate was 1.3 mm/minute.

Shear strengths were calculated using the simple formula:

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

Where:

S_u = Ultimate shear strength, MN/m^2

V = Load at failure, N

t = Specimen thickness, mm

b = Specimen width, mm

E.9 FLEXURAL PROPERTIES OF COMPOSITES

The cured composites were machined into flexural specimens 1.3 cm wide by 13-cm long and tested in flexure at a single mid-span loading point using a 32:1 span-to-depth ratio. Loading rate was 1.3 mm/minute.

Flexural strengths and moduli were calculated using the formula:

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

and

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

Where:

F_u = Stress in the outer fiber at mid-span, MN/m^2

E_b = Modulus of elasticity in bending, GN/m^2

P = Load at failure, N

L = Span, inch

b = Width of specimen, mm

d = Thickness of specimen, mm

m = Slope of the tangent to the initial straightline portion of the load deflection curve, N/mm

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