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DEVELOPMENT OF AUTOCLAVABLE POLYIMIDES

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

TRW
SYSTEMS GROUP

ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NASA Lewis Research Center
Contract NAS3-17770

Tito T. Serafini, Project Manager

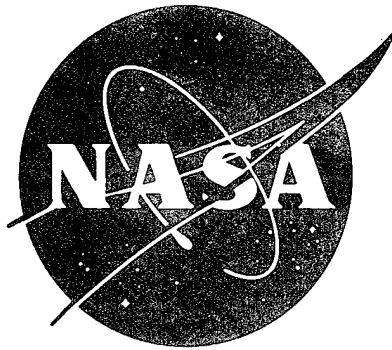
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16. Abstract A poly(Diels-Alder) (PDA) resin approach was investigated as a means to achieve autoclavability of high temperature resistant resin/fiber composites under mild fabrication procedures. The results of the study were highly promising and program objectives were achieved. Low void content Type A-S graphite reinforced composites were autoclave fabricated from a PDA resin/fiber prepreg prepared from an acetone:methanol:dioxane varnish. Autoclave conditions were 477°K (400°F) and 0.7 MN/m ² (100 psi) for up to two hours duration. After postcure at temperatures up to 589°K (600°F), the composites demonstrated high initial mechanical properties at temperatures up to 561°K (550°F). The results from isothermal aging studies in air for 1000 hours indicated potential for long-term (>1000 hours) use at 533°K (500°F) and shorter-term (up to 1000 hours) at 561°K (550°F).					
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FOREWORD

This document constitutes the final report for the work accomplished between 26 June 1973 and 30 June 1974 by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-17770 on Development of Autoclavable Polyimides.

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

The Applied Chemistry and Materials Technology Departments of the Chemistry and Materials Technology 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 NAS3-17770. The objective of this program was to develop addition-type polyimide resins which could be processed at a maximum of 477°K (400°F) and 1.4 MN/m² (200 psi) for use as matrix resins in high temperature resistant resin/fiber composites. The program objective was accomplished by sequential program tasks which included 1) model compound studies and polymer synthesis and characterization, 2) autoclave process screening, 3) resin/process reproducibility studies and 4) detailed long-term testing of autoclave fabricated composites.

The first phase of the work involved mechanism studies of a model compound simulating the structure of polymers prepared by a poly(Diels-Alder) (PDA) method which was shown previously in Contract NAS3-15834 to autoclave process at temperatures near 477°K (400°F). Although prior polymerization studies gave strong evidence that intermediate resin structures undergo *in situ* aromatization at temperatures up to 589°K (600°F), a different behavior was observed in the model study. The model compound did not give the expected aromatic structures at temperatures up to 589°K. Instead, products were obtained which apparently resulted from a complex set of reactions including homopolymerization of the maleic species formed by a reverse Diels-Alder reaction. This behavior was not observed in subsequent polymer studies and it was concluded that the model compound was not of sufficient molecular weight or had a molecular structure non-representative of PDA polymers.

The major emphasis in Task I was placed on detailed investigation of the poly(Diels-Alder) (PDA) polymerization reaction of bis(furanimide)

compounds and bis(maleimides) at temperatures of approximately 477°K (400°F). Postcure studies at temperatures up to 589°K then were conducted on the resin products initially cured. The studies showed that a combination of bis(furfuryl) benzophenone tetracarboxylic imide (BFBI) and bis(4-maleimido-phenyl) methane (BMPM) gave neat polymers meeting program thermo-oxidative stability objectives [i.e., 561°K-589°K (550°F-600°F)].

The results of the polymer study were employed to structure autoclave fabrication process matrices. Screening studies were conducted and process variable levels within program goals were conducted in an autoclave employing Hercules A-S fiber as a reinforcement. During processing studies, dimethyl formamide (DMF), N-methylpyrrolidinone (NMP) and solvent mixtures prepared from dioxane were evaluated as varnish solvents. Autoclave conditions suitable to prepare low void content laminates possessing high initial mechanical strengths at room temperature (R.T.) and 561°K (550°F) were identified employing a prepreg prepared from a tersolvent consisting of a 1:1:1 by weight mixture of acetone, methanol and dioxane.

Further studies of the resin and process in the tersolvent indicated that purity of the BMPM used in the PDA reaction and the postcure cycle were of critical importance to obtaining composites with high initial and retained mechanical strengths and low void contents. Composites of up to 254-mm (10.00-inches) x 292-mm (11.50-inches) x 3.2-mm (0.12-inch) were then produced for detailed testing studies described below.

In the final phase of the program, mechanical properties of composites prepared by the PDA approach were determined before, during and after isothermal aging of specimens at 533°K (500°F) and 561°K (550°F) in air for 1000 hours. Retention of properties after the aging period gave strong evidence that the PDA system is suitable for $\leq 477^\circ\text{K}$ (400°F) and 0.7 MN/m² (100 psi) autoclave fabrication of composites possessing useful long-term properties at 561°K (550°F).

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I. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-17770, during the period of 26 June 1973 through 25 June 1974. This program consisted of experimental studies to develop low temperature [477°K (400°F)], low pressure [0.7 MN/m² (100 psi)] curing, autoclavable polyimides. The studies consisted of detailed evaluation of a poly(Diels-Alder) (PDA) reaction which was shown to be promising in Contract NAS3-15834 (Reference 1) as a lower temperature curing resin alternative to pyrolytically polymerizable polymers. The autoclavable resins are intended for use as matrix resins in high performance graphite fiber reinforced airframe structural components.

The concept investigated in this program concerned development of a viable alternative resin system to the A-type or pyrolytically polymerization resins. It was shown in Contract NAS3-15834 (Reference 1) that the A-type polymers discovered in Contract NAS3-7949 (Reference 2) would not cure at the 477°K temperature objective. As a result, a new approach which incorporates a novel polymerization/aromatization reaction sequence and was developed under Independent Research and Development funds at TRW Systems (Reference 3) was investigated in Contract NAS3-15834 (Reference 1). This approach is similar in nature to the polymerization of monomeric reactants (PMR) approach developed at NASA/Lewis Research Center (Reference 4) in that monomeric type ingredients are employed directly, but differs significantly in the polymerization method.

The new 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 below 477°K (400°F) to give initially an oxygen bridged six-membered ring polymers which subsequently undergo *in situ* thermal aromatization through loss of a mole of water to give aromatic polyimide structures. It was experimentally shown that the most 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 ratio. Parallel mechanism studies to resin screening were conducted in attempts to verify the postulated *in situ* aromatization reaction. However, conclusive experimental evidence verifying this reaction was not obtained from the model compound employed.

Fabrication studies were conducted on the PDA resin consisting of BFBI and BMPM. Attempts to reproduce preliminary data obtained from composites prepared from Type A-S fiber and dimethyl formamide (DMF) solvent (Contract NAS3-15834), as well as investigations employing N-methylpyrrolidinone (NMP) as the laminating solvent, were unsuccessful. The composites prepared using DMF and NMP as solvents had high void contents (>5% w/v) and low [49.9 MN/m² (7100 psi)] interlaminar shear strengths.

Consequently, studies were then conducted to identify a solvent system yielding prepreg of acceptable quality [i.e., sufficient tack and drape and processability (drying behavior similar to or improved over DMF)] which would yield autoclaved composites of high initial properties at R.T. and at 561°K (550°F) or greater. A tersolvent combination consisting of acetone, methanol and dioxane in a 1:1:1 by weight ratio was found to provide the improved system.

Studies were then conducted to establish the reproducibility of the BFBI/BMPM combination, the tersolvent and selected autoclave process. The criteria used for judgment of reproducibility were high composite mechanical properties and low (<2%) void contents as determined by calculated values and ultrasonic (C-scan) measurements. It was shown that the purity of the BMPM ingredient and a staged postcure cycle from 477°K (400°F) to 589°K (600°F) are critical to obtain reproducible composites possessing 70.0 MN/m² (10,000 psi) shear strengths and 1750 MN/m² (250 ksi) flexural strengths of which 70% retention was obtained initially at 561°K (550°F).

The most promising resin/solvent/process was used to prepare Hercules Type A-S graphite fiber reinforced composites for detailed testing. Property data obtained before, during and after 1000 hours isothermal aging in air at 533°K (500°F) and 561°K (550°F) gave strong evidence that BFBI/BMPM A-S composites are suitable for use at these temperatures for long durations. These test results gave insight into plausible PDA ingredient modifications which yield zero defect autoclaved parts suitable for use at 589°K (600°F).

This report is divided into four sections covering the program technical tasks: 1) (Task I) - Polymer Synthesis and Characterization, 2) (Task II) - Process Development and Evaluation, 3) (Task III) - Reproducibility Studies

and 4) (Task IV) - Final Composite Characterization. The significant conclusions 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 - POLYMER SYNTHESIS AND EVALUATION

The objective of this task was to prepare and evaluate new resin compositions specifically designed to improve the processability and thermo-oxidative stability of the poly(Diels-Alder) (PDA) derived addition-type polyimide resins developed in Contract NAS3-15834. Additionally, a more thorough understanding of the mechanism of the *in situ* dehydration of the oxygen-bridged intermediate in the poly(Diels-Alder) (PDA) reaction was sought.

The mechanism study was conducted on a simple model compound selected to be representative of the bridged adduct intermediate in the poly(Diels-Alder) (PDA) reaction. The model compound was subjected to a number of simulated processing conditions and the resulting products were characterized by spectroscopic methods. Details of this study are presented in Section 2.1.

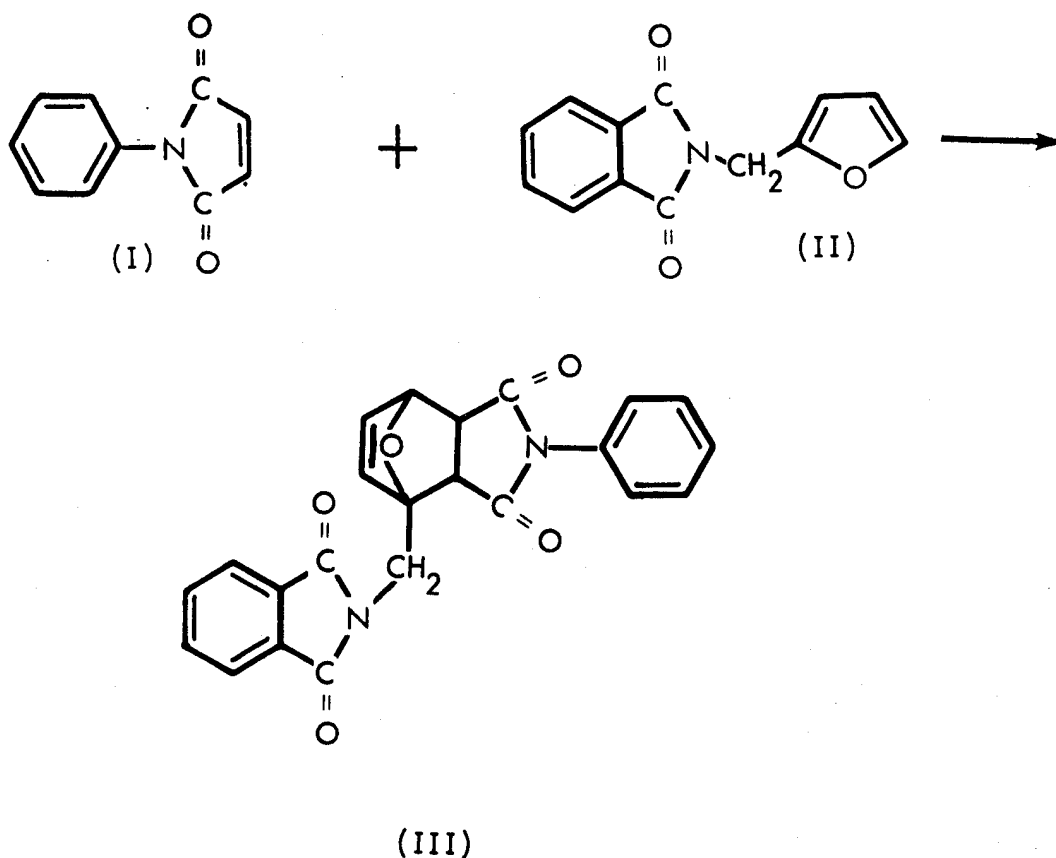
The results obtained in Contract NAS3-15834 demonstrated that the PDA approach showed excellent promise to provide autoclave fabricated, high modulus graphite reinforced composites. However, it also was evident that additional resin development studies were necessary to achieve optimum combinations of mechanical properties and processability. Consequently, studies were conducted on a modified resin system specifically tailored to meet the program objectives. The most significant result of the resin studies was the finding that the mixture of bis(4-maleimidophenyl) methane (BMPM) and bis(2-furfuryl) benzophenone tetracarboxylic imide (BFBI) monomers can be cured at temperatures as low as 450°K (350°F). The results of the resin studies are described in Section 2.2.

2.1 MECHANISM STUDIES

The mechanism study of the poly(Diels-Alder) (PDA) reaction was undertaken in an attempt to understand more fully the chemistry of this polymer system. This basic understanding of the chemistry was sought to aid in the optimization of the PDA resins and to help in the selection of a processing cycle. The studies were conducted using a simple model compound whose structure was selected to simulate the simplest PDA adduct. A description of these studies is given in the following sections.

2.1.1 Preparation and Characterization of Model Compounds

The model compound selected for this mechanism study was the Diels-Alder adduct of N-phenyl maleimide (I) and N-furfuryl phthalimide (II), specifically compound III obtained according to the equation below. Compounds I and II were prepared by normal synthesis procedures which are described in Appendix A.1. Both model precursors, after synthesis, were characterized by infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy (see Appendix A.1).

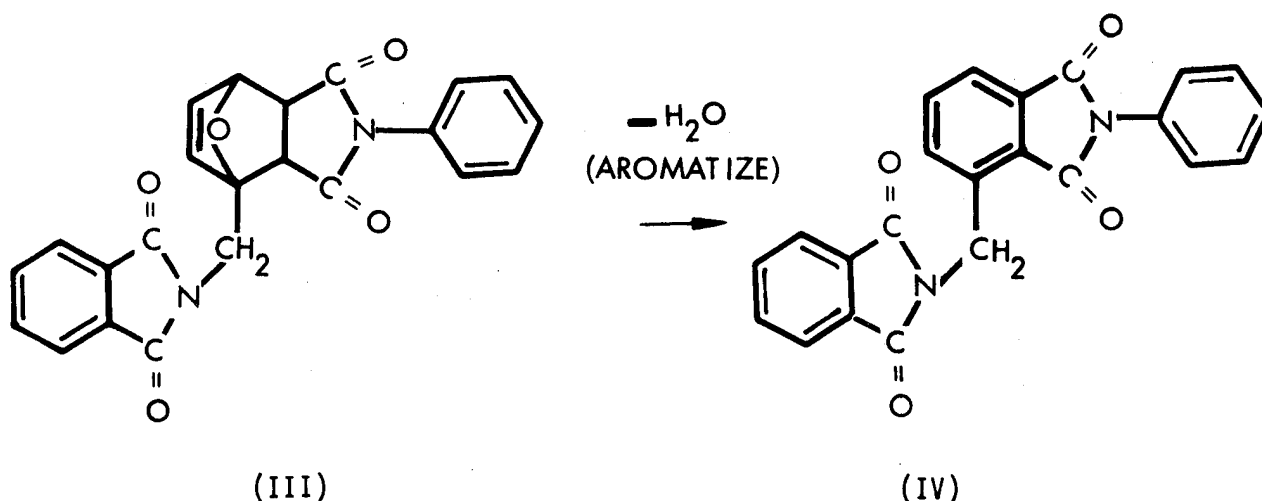


The Diels-Alder adduct, compound III, was prepared by heating an equal molar mixture of I and II in solution. Three different solvents were evaluated for use in this reaction, namely ethanol, ether and toluene. All three solvents gave some adduct as indicated by thin layer chromatography (tlc), but ethanol was found to be the best solvent. Simply refluxing a solution of I and II in ethanol for 18 hours gave the adduct

as a colorless precipitate in 80% yield. The adduct was characterized by ir and nmr analysis. The spectra may be found in Appendix A.1. The ir spectrum contains two carbonyl bands at 1715 and 1775 cm^{-1} , indicative of the presence of imide. To permit comparison of the ir spectra of the adduct and the starting materials (I and II), an equimolar blend (physical mixture) of I and II was prepared and an ir was obtained (Figure A.4). The significant difference between the spectra is in the 1200 cm^{-1} region. The ir spectrum of the adduct has a very strong band at 1190 cm^{-1} which does not appear to any great degree in the spectrum for the blend of I and II. This new band was ascribed to the oxybridge, as supported by the fact that alicyclic ethers generally display a band in the 1200 cm^{-1} region (Reference 5). The nmr spectrum (Figure A.6) for the oxygen bridged adduct, III, is also consistent for the structure and the band assignments are discussed in detail in Appendix A.1.

2.1.2 Mechanism Study of *in situ* Aromatization

Studies were conducted on the postulated *in situ* aromatization of the oxygen bridged model Compound III to Compound IV as shown below. The first experiment performed with the model Compound III was to subject it to thermogravimetric analysis (TGA) in nitrogen. This experiment was conducted in order



to determine weight loss (postulated to be loss of water) as a function of temperature. The theoretical weight loss expected for the dehydration step is 4.5% w/w. However, the TGA scan obtained for Compound III

showed no perceptible weight loss until 448°K and then a sudden loss (ca. 80%) occurred. The 448°K temperature corresponds closely to the melting point of the adduct (see Appendix A.1) and the observed weight loss was attributed to the liquid vaporizing in the air stream rather than the occurrence of the desired dehydration reaction.

Differential scanning calorimetry (DSC) also was employed in an attempt to define the temperature range where the postulated dehydration occurs. However, the results of the DSC study also were not useful in determining the temperature at which dehydration begins or becomes significant. Above the melting point (448°K), there were no definitive endotherms or exotherms observed in the DSC scan. Consequently, it was concluded that for the model compound, the dehydration probably takes place over a broad temperature range rather than occurring at a particular temperature or narrow temperature range.

An experimental matrix (Figure 1) then was designed for subjecting the oxygen bridged adduct (III) to simulated autoclave conditions. The experimental procedure used for this work was identical to that employed during the PDA resin work on Contract NAS3-15834 (Reference 1). All residues produced during this work were glassy solids and were found to be soluble (>15% w/w) in DMF and chloroform. Weight losses of the samples were determined at the end of the heating cycle. The results obtained from this study are presented in Table I.

TEMPERATURE	TIME, HR		
°K/°F	2	4	6
450/350	X	X	X
464/375		X	X
477/400	X	X	
505/450	X	X	

Figure 1. Experimental Matrix to Study
In Situ Aromatization on Model Compound

TABLE I
RESULTS OF *IN SITU* AROMATIZATION STUDY ON MODEL COMPOUND

Experimental Conditions ^a		Weight Loss After Heating, % w/w
Temperature °K/°F	Time, Hr.	
450/350	2	2.41
	4	1.87
	6	3.71
464/375	4	2.77
	6	5.71
477/400	2	3.09
	4	4.44
505/450	2	5.18
	4	11.43 ^b

^aOther conditions, pressure 0.7 MN/m² (100 psi)

^bSome sample lost during experimentation

The weight loss measurements presented in Table I were interpreted to indicate that the desired aromatization reaction was occurring to some extent over the entire temperature range. It was assumed that the observed weight loss could be used as a measure of the degree to which the desired dehydration reaction had occurred. However, when the pyrolysis residues were characterized by nuclear magnetic resonance (nmr) spectroscopy, it was shown that this assumption was incorrect and that the dehydration reaction had not occurred to a significant extent. A discussion of these findings is given below.

The nmr spectra for a number of the pyrolysis residues are shown in Figure A.6 through Figure A.9 (see Appendix A.1). The nmr spectra are arranged such that the effects of temperature and time are clearly illustrated. For example, the spectrum obtained from the pyrolysis residue heated at 450°K

(350°F) for 2 hours is shown in Figure A.6 . The important features in the spectrum are the appearance of two bands at 3.77 τ and 5.25 τ . These bands are appropriate for the protons on the furan ring and the methylene protons, respectively, for N-furfuryl phthalimide (Compound II). The formation of Compound II is attributed to the occurrence of a reverse Diels-Alder reaction during the pyrolysis run. Additional evidence that the reverse Diels-Alder reaction occurred was obtained from the spectra of the pyrolysis residues run at higher temperatures.

The spectra for the residues heated to 464°K (375°F) for 4 and 6 hours clearly illustrate that as the duration of heating is increased, the band at 6.95 τ becomes less intense and, at the same time, the band at 5.25 τ increases in intensity. In addition, the other bands in the spectra attributed the oxybridged adduct (III) become less intense as time is increased giving further evidence that the amount of the adduct is decreasing.

The same results were observed for the samples pyrolyzed at 477°K (400°F). The upfield band at 6.98 τ becomes less intense while the 5.25 τ band increases in intensity. Finally, the nmr spectrum (Figure A.9) for the sample heated at 505°K (450°F) for 2 hours shows that under these conditions the adduct (Compound III) is completely converted to Compound I and Compound II.

The pyrolysis residues also were analyzed by infrared (ir) spectroscopy. Limited information was obtained from the spectra because only minor changes could be detected. The most useful information obtained from the ir spectra did show the relative intensity of the band at 1190 cm^{-1} decreases as time and temperature are increased. This band was assigned to the oxygen bridge of the adduct and the decrease in intensity of this band supports the conclusion reached earlier from the nmr data that the amount of oxybridged adduct does decrease as temperature and time are increased.

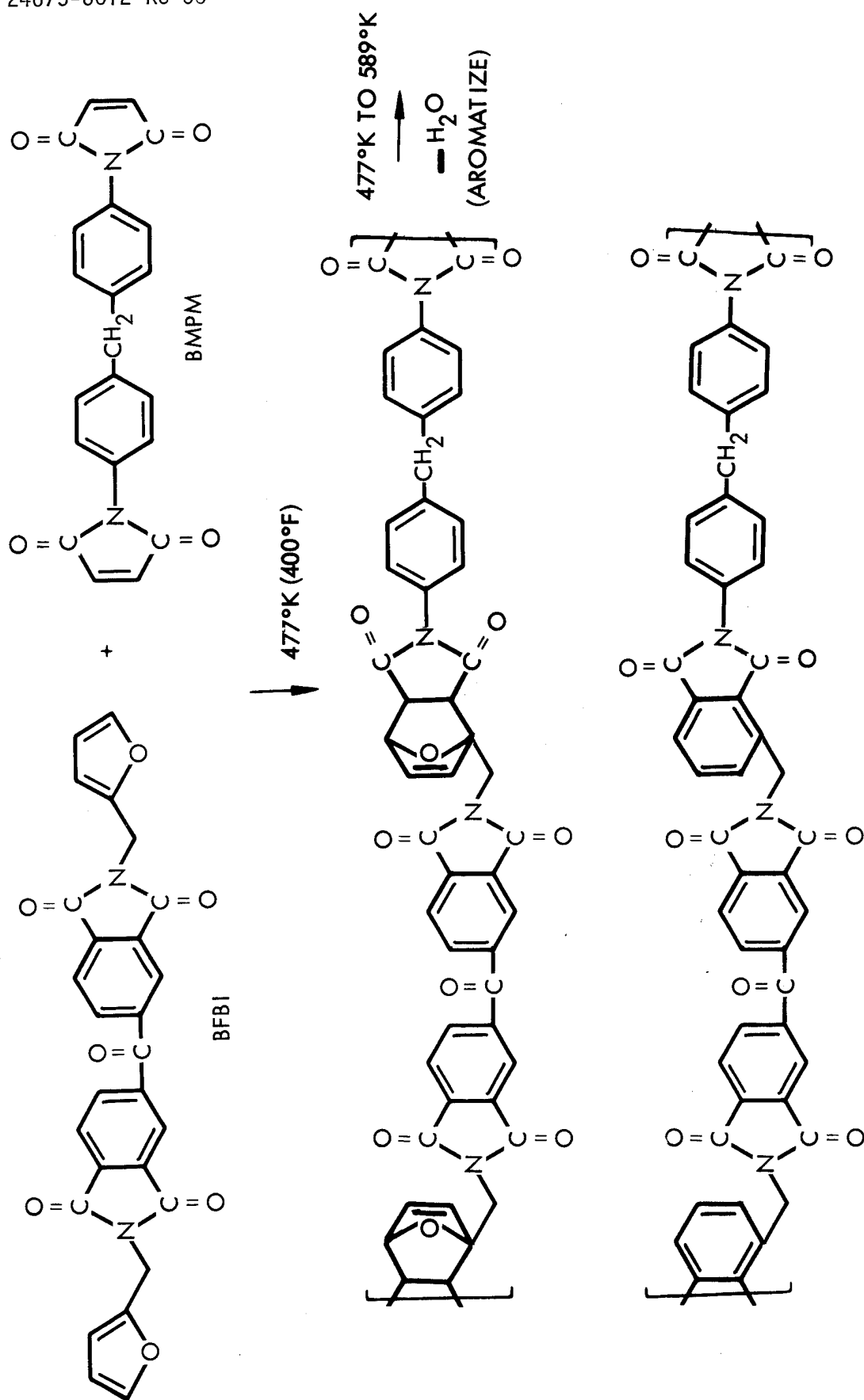
Additional data also were gained during this work by trapping the effluents of selected pyrolysis runs. In a typical run, after the heating period was complete, the nitrogen used to pressurize the system was passed through a cold trap (acetone/dry ice) and then a moderate vacuum was applied to the pyrolysis apparatus to remove any additional volatile matter. The contents of the cold traps were analyzed by mass spectroscopy (ms) and found to be water. However, the quantity of water trapped during a typical pyrolysis run was a very small fraction of the theoretical amount. For example, the

5 mg of water collected from the sample pyrolyzed at 505°K (450°F) for 2 hours accounts for ca. 1% of the theoretical amount of water to be evolved during aromatization. The results of the trapping experiments obtained for the model compound are in sharp contrast to those obtained for the PDA resin derived from BMPM and bis(2-furfuryl) pyromellitimide (BFPI). During work performed on Contract NAS3-15834, it was found that the amount of water trapped under identical pyrolysis and trapping conditions accounted for ca. 20% (w/w) of theoretical indicating that the aromatization reaction was occurring to some degree. Additional water also was lost during postcure of the PDA resin to give over 80% (w/w) of theoretical amount water.

The failure to observe the postulated and desired *in situ* dehydration of the model oxybridged adduct (III) was very disappointing in view of observations made during previous experimental work on the PDA-type resins in Contract NAS3-15834. As was stated above, in the previous work using polymeric material, up to 80% of the theoretical amount of water from *in situ* aromatization of the oxygen bridge was isolated and identified. Also, and of greatest significance, resins derived from PDA-type polymerizations demonstrated excellent weight and property retention at 561°K (550°F) in air for 1000 hours. Therefore, it is strongly believed that the primary linkage resulting from the PDA approach is substantially aromatic in character because of the superior high temperature performance established in Contract NAS3-15834 for PDA resins.

2.2 RESIN MODIFICATION STUDIES

The resin modification studies were conducted in order to find a PDA resin which possessed the optimum combination of thermo-oxidative stability/processability/mechanical property characteristics. The reaction sequence developed in Contract NAS3-15834 to form the PDA resin from BFBI and BMPM is shown on the following page. These ingredients polymerize at or below 477°K (400°F) to give initially an oxygen bridged six membered ring polymer which undergo *in situ* thermal aromatization through loss of water to give aromatic polyimide structures. The studies performed in this program included the examination of the effect of cure temperature and/or postcure cure time on the simplest PDA resin from BFBI/BMPM. A new PDA resin also was prepared which contained unsaturated sites in the backbone for subsequent use in preparing a crosslinked PDA resin. These studies are described in the following paragraphs.



2.2.1 BFBI/BMPM Cure Studies

Experimental studies were conducted to evaluate the use of lower cure temperatures [below 474°K (400°F)] for the PDA approach employing BFBI and BMPM. In this study, a stoichiometric mixture of BFBI/BMPM ingredients was cured for four hours at 1.4 MN/m² (200 psi) at each of the following temperatures: 450°K (350°F), 464°K (375°F) and 474°K (400°F). Each polymer sample obtained from the above cure conditions was a well consolidated plug indicating that melt and flow occurred before final cure. However, a sample heated at 436°K (325°F) failed to melt and flow indicating 450°K (350°F) is near the lowest cure temperature for this system.

The polymer samples (plugs) obtained above were subsequently postcured in a forced-air oven employing a postcure cycle which consisted of a four-hour linear heat-up rate from 477°K (400°F) to 589°K (600°F) followed by heating at 589°K for four hours. The results of this experimentation are given in Table II. As can be seen in Table II, the samples display very little difference in thermo-oxidative stabilities indicating that cure temperatures as low as 450°K are useful for this system. The postcured samples then were evaluated for long-term thermo-oxidative stability by isothermally aging them for 300 hours at 533°K (500°F) and 561°K (550°F). The results of the aging study are presented in Table V in Section 2.2.4.

TABLE II
SUMMARY OF CURE STUDIES ON BFBI/BMPM MIXTURE^a

Cure Temperature (°K/°F) ^b	Weight Loss During Cure (% w/w)	Temperature of Initial Weight Loss in TGA (°K/°F) ^c
450/350	0.75	623/662
464/375	0.34	611/640
474/400	1.3	611/640

- a. Employing stoichiometric mixture of BFBI/BMPM ingredients.
- b. Other cure conditions; 4 hours and 1.4 MN/m² (200 psi).
- c. Scan rate 3°K/min. and air flow 100 ml/min.

2.2.2 Postcure Studies on BFBI/BMPM Resin

Concurrent with the cure temperature studies described above, experimental studies were conducted to determine the effect of postcure conditions on the BFBI/BMPM resin. This information was sought to supplement the data which were originally generated in Contract NAS3-15834. The results were to be used ultimately to help in the selection of a postcure cycle for the composites prepared in Task II studies.

For the postcure studies, the monomers were cured employing the same polymerization conditions as used in Contract NAS3-15834, namely a cure duration of four hours at 505°K (450°F) and 1.4 MN/m² (200 psi). The resin samples were subsequently postcured as solid plugs in a forced air oven employing a cycle which consisted of a four-hour linear heat-up rate from 477°K (400°F) to 589°K (600°F) followed by heating at 589°K for one, two, four, eight, eighteen, twenty-four and forty-eight hours. The residues then were subjected to thermogravimetric analysis. The results of this experimentation are summarized in Table III.

The results presented in Table III show that all the postcured samples exhibit essentially the same initial thermo-oxidative stability (ITOS) as measured by TGA. A small increase in ITOS ($\sim 10^{\circ}\text{K}/18^{\circ}\text{F}$) was observed in the samples postcured for eight and eighteen hours. However, as the postcure cycle was extended beyond eighteen hours, the neat resin samples displayed a reduced ITOS. In addition, the samples continued to lose weight as the postcure cycle was extended indicating that the observed weight losses could not be entirely attributed to the desired loss of water during aromatization. It appeared from these results that the neat resins decompose after relatively short exposure times at 589°K (600°F) in air. From the results of this experimentation and results obtained on Contract NAS3-15834 a postcure time of four to six hours at 589°K (600°F) was selected for subsequent postcure of neat resin and composite samples during the remainder of the program.

2.2.3 Crosslinked PDA Resin

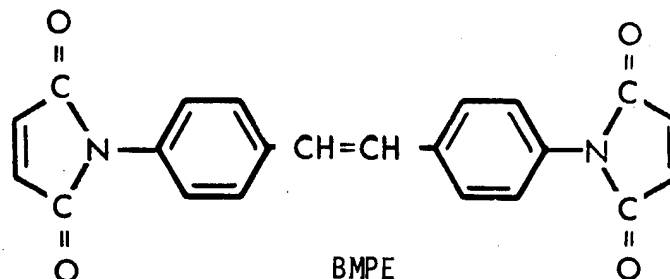
Experimental studies on the resin modification were focused on developing improved PDA resins. The objective of this work was to introduce thermally stable crosslinks into the PDA resin matrix to improve its thermo-oxidative and mechanical property characteristics. The method selected was to introduce unsaturation into the linear PDA resin

TABLE III
RESULTS OF POSTCURE STUDIES ON BFBI/BMPM MIXTURE^a

Postcure Duration, hr. ^b	Weight Loss During Postcure (% w/w)	Temperature of Initial Weight Loss in TGA Postcured Resin (°K/°F) ^c
1	1.04	623/662
2	1.33	623/662
4	1.56	623/662
8	1.92	633/680
18	2.55	633/680
24	4.42	598/617
48	7.00	585/592

- a. Employing a stoichiometric mixture of BFBI/BMPM ingredients cured 4 hours at 505°K (450°F) and 1.4 MN/m² (200 psi).
 b. Postcure cycle consisted of a 4 hour linear heat-up from 477°K (400°F) to 589°K (600°F) followed by heating at 589°K (600°F) for stated time.
 c. Scan rate 3°K/min. and air flow 100 ml/min.

for subsequent use as a crosslinking site. The monomer selected for introducing the desired unsaturation was bis(4-maleimidophenyl) ethylene (BMPE) (for preparation see Appendix B.3). This maleimide was primarily selected because it can be employed in the PDA reaction scheme in the same fashion as BMPM. The monomer also has the added feature that any desired level of crosslink can be obtained by simply substituting BMPE for some of the BMPM and adding the appropriate amount of crosslinking agent. The unsaturated ethylene group was expected to undergo a Diels-Alder reaction with BFBI to give a benzene ring by eliminating water through a typical PDA reaction. Thus, in this case, the BFBI serves as the chain extender and also as the crosslinking agent.



Two different resin samples were prepared employing BMPE and the BFBI/BMPM couple. The first sample was a linear PDA resin containing BMPE as indicated by the following formulation BFBI/90BMPM:10BMPE. The second sample was a linear PDA resin formulation containing BMPE to which additional BFBI (crosslinking agent) was added (according to the following formulation BFBI/90BMPM:10BMPE + 5BFBI) to give a crosslinked resin. Both samples were cured at 505°K (450°F) for 4 hours and 1.4 MN/m² (200 psi). The resultant cured samples then were subjected to thermogravimetric analysis. The results of this work are shown in Table IV. The samples then were postcured employing a 4-hour linear heat-up from 472°K to 589°K followed by heating at 589°K for 4 hours (these cure and postcure conditions were employed for the neat PDA resin work on Contract NAS3-15834). The resin samples then were isothermally aged at 533°K (500°F) and 561°K (550°F) for 300 hours at the same time the BFBI/BMPM samples (prepared in Section 2.1.1) were aged. The results of the aging are given in the next section.

TABLE IV
 CHARACTERIZATION OF BMPE CONTAINING PDA RESINS

Polymer Formulation ^a	Temperature of Initial ^b Weight Loss in TGA (°K/°F)
BFBI/90BMPM:10BMPE	623/662
BFBI/90BMPM:10BMPE + 5 BFBI	623/662

- a. Cured at 505°K (450°F) for 4 hours and 1.4 MN/m² (200 psi).
- b. Scan rate 3°K/min. and air flow 100 ml/min.

2.2.4 Isothermal Aging of Neat Resins

The neat PDA resins cured at lower temperatures and the BMPE containing resins were isothermally aged for 300 hours at 533°K (500°F) and 561°K (550°F) in a forced-air oven. The samples were periodically weighed during the aging and the results are presented in Table V and the 561°K results are shown graphically in Figure 2. No significant change in physical appearance of the samples was noted after the 300-hour aging period.

TABLE V
ISOTHERMAL AGING OF NEAT PDA RESIN SAMPLES
AT 533°K AND 561°K

Sample Composition	Cure Conditions ^a		Weight Percent Loss - Duration Points in Hours											
	Duration, hr	Temperature (°K/°F)	48 hr		97 hr		144 hr		234 hr		300 hr			
			533°K	561°K	533°K	561°K	533°K	561°K	533°K	561°K	533°K	561°K		
BFBI/BMPM	4	450/350	b	1.02	0.43	1.49	0.74	1.83	1.07	2.64	1.24	2.97		
BFBI/BMPM	4	464/375	b	1.06	0.60	1.67	0.88	2.08	1.17	3.08	1.36	3.45		
BFBI/BMPM	4	474/400	b	1.22	0.69	1.78	0.98	2.30	1.34	3.52	1.55	4.00		
BFBI/90BMPM:10BMP	4	505/450	b	1.19	0.50	1.61	0.77	2.01	1.05	2.79	1.27	3.15		
BFBI/90BMPM:10BMP + 5BFBI	4	505/450	b	1.16	0.54	1.58	0.80	2.03	1.16	2.81	1.32	3.12		

a. Postcure cycle consisted of 4 hour linear heat-up from 472°K (400°F) to 589°K (600°F) followed by isothermal cycle at 589°K for 4 hours.

b. Not determined

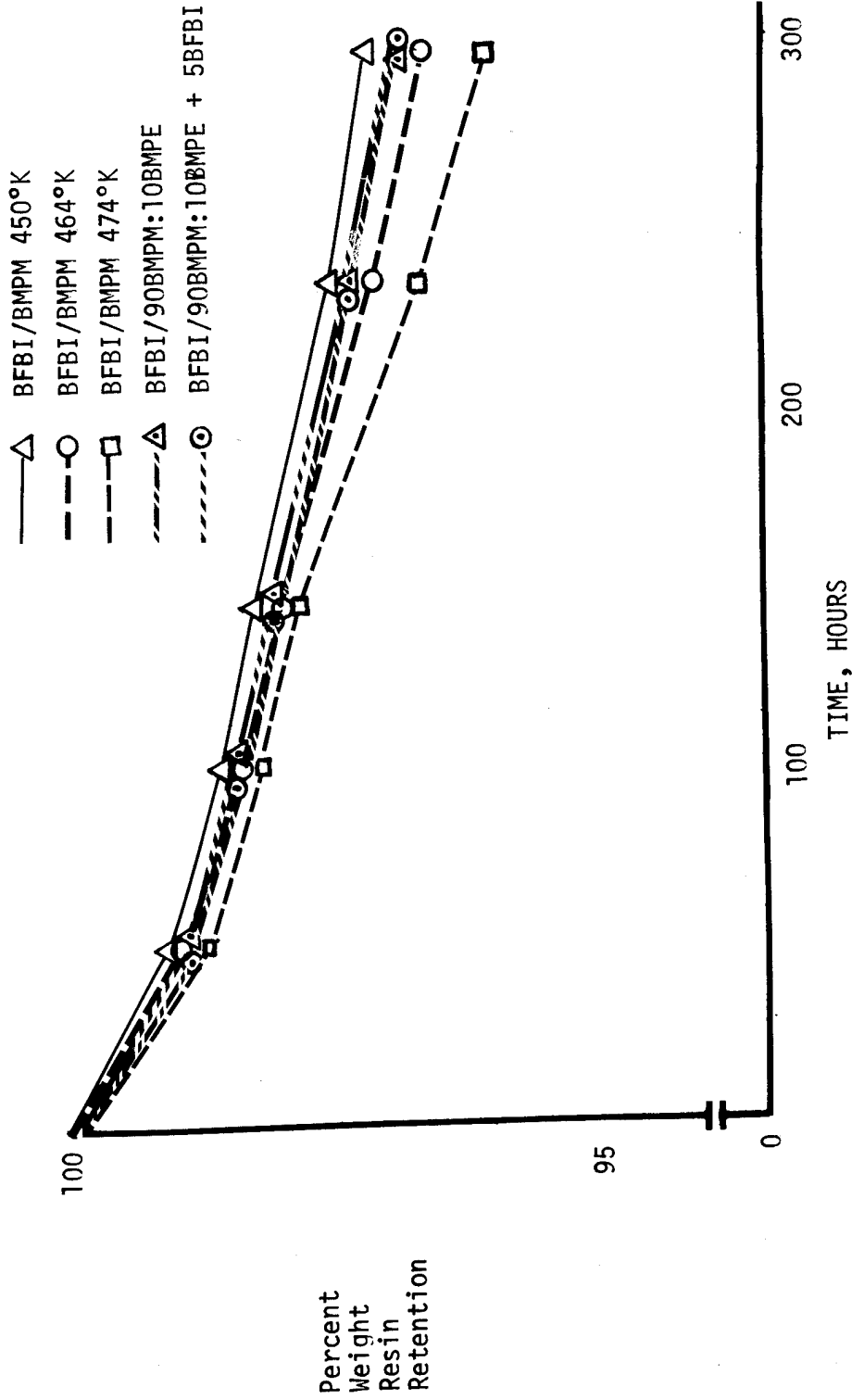


Figure 2. Isothermal Aging of Neat PDA Resin Samples at 561°K (550°F)

The aging experiment demonstrated several significant factors concerning the resin samples and the cure conditions used to prepare the samples. General conclusions based on the results of the aging are as follows:

- All resins studied show promise for long-term use at 533°K (500°F) and 561°K (550°F)
- The PDA resins (BFBI/BMPM) cured at lower temperatures (i.e., 450°K and 464°K) displayed improved thermo-oxidative stability over the PDA resin cured at 474°K (400°F)
- The BFBI/BMPM resins containing BMPE cured at 505°K (450°F) showed thermo-oxidative stability comparable to neat resins cured at 450°K (350°F).

A more detailed discussion of the results is presented in the paragraphs that follow.

The data presented in Table V show that all samples exhibit outstanding stability at 533°K during the aging period studied. Essentially no difference in thermo-oxidative stability as measured by weight loss was noted at 533°K and the resins show promise for long-term use at this temperature. However, the aging data at 561°K showed reasonable differences in thermo-oxidative stability between the resin samples as discussed below.

It was interesting to note that the BFBI/BMPM sample cured at the lowest temperature [450°K (350°F)] displayed the greatest thermal stability of all the samples. As the cure temperature for this couple was increased, the resulting polymer samples displayed a loss in thermo-oxidative stability. The BMPE containing PDA resin displayed thermo-oxidative stability that was nearly equivalent to that of the BFBI/BMPM resin sample cured at 450°K. Essentially no difference in stability was noted for the two BMPE containing resins. This result was somewhat surprising because one sample was formulated to be a linear polymer and the other sample was formulated to give a cross-linked system. However, because the BFBI crosslinking agent was present in the linear formulation, there is high probability that some crosslink formation occurred in the resin matrix even though it was formulated to be linear. Therefore, since both samples probably possessed a certain degree of cross-link character, their thermo-oxidative stability appeared equivalent. Nevertheless, the BMPE containing resins did show high promise for use at 561°K based on the aging data and they were evaluated as possible resin candidates in Task II composite fabrication studies.

2.2.5 Precure Study on BFBI/BMPM Resin

A investigation was conducted at the end of the Task I studies to examine the effects of temperature and time on the BFBI/BMPM system below 450°K (350°F) (the lowest effective cure temperature). This information was sought to help in structuring the prepreg cycle and/or the autoclave cure cycle for the BFBI/BMPM system.

The BFBI/BMPM mixture was heated in a forced-air oven at atmospheric pressure for the time durations and temperatures given in Figure 3.

Staging Temperature °K (°F)		Staging Duration in Hours				
		1	2	4	8	16
394	(250)				X	X
405	(270)			X	X	
416	(290)		X	X		
427	(310)	X	X			
439	(330)	X				

Figure 3. Precure Matrix For BFBI/BMPM Mixture

Each sample obtained from this experimentation then was characterized as follows:

- Percent (w/w) solubility in NMP
- Inherent viscosity
- Cure at 450°K (350°F) for two hours to measure flow and consolidation properties of the resin.

The results obtained from this experimentation are given in Table VI.

The results indicated that a small increase in the inherent viscosity of the BFBI/BMPM mixture was obtained as the temperature was increased or as the time duration was increased at a given temperature. In addition to molecular weight build-up, a crosslinking reaction appears to become significant at 427°K (310°F). The resin samples obtained at 427°K and 439°K (330°F) were found to be partially soluble (ca. 90%

dissolved) at 30% (w/w) in NMP indicating formation of a high molecular weight and/or a crosslinked resin. Dilution to 5% (w/w) with additional NMP failed to yield a solution and subsequent heating of the mixtures to reflux for one hour also did not give a solution at 5% solids. These results showed that in the neat resin system some crosslinking does take place at temperatures as low as 427°K. The crosslinking reaction may be favored at these temperatures in the neat resin because full melt and flow

TABLE VI
SUMMARY OF PRECURED RESIN PROPERTIES

Precure Temperature (°K/°F)	Precure Duration (Hours)	Weight Loss (% w/w)	Solubility in NMP at 293°K (% w/w)	Inherent Viscosity (in NMP) at 303°K
394/250	8	0.40	> 30	a
	16	0.47	> 30	0.04
405/270	4	0.46	> 30	0.03
	8	0.54	> 30	0.04
416/290	2	0.55	> 30	0.04
	4	0.62	> 30	0.05
427/310	1	0.58	b	0.05
	2	0.64	b	c
439/330	1	0.50	b	c

- a - Not determined.
- b - Most of sample dissolved at 30% (w/w) solids; insolubles still present when diluted to 1% w/w solids.
- c - Not determined due to insolubles in solution.

does not occur to give a homogenous mixture thus resulting in local areas of high concentration of bis(maleimide). Subsequent homopolymerization of some of the bis(maleimide) (BMPM) would yield the observed insoluble material. Somewhat different behavior is expected for this system when solvent is employed as in composite fabrication because local areas of

high concentration of bis(maleimide) are much less likely and it is postulated that the Diels-Alder reaction would be more highly favored than the homopolymerization reaction, thus resulting in the formation of high molecular weight resins.

All of the precured samples displayed the desired melt and flow characteristics upon cure at 450°K (350°F) for a two-hour duration. The polymer samples obtained were well consolidated plugs and appeared to be homogenous in character. It was concluded from this study that temperatures up to ca. 422°K (300°F) could safely be employed in prepreg processing or in the autoclave precure cycle. This information was used in Task II studies described in the next section.

III. TASK II - COMPOSITE FABRICATION AND PRELIMINARY CHARACTERIZATION

The objective of this task was to develop and refine autoclave molding processes for the poly(Diels-Alder) (PDA) type polyimide resin. It was demonstrated during this task that the PDA derived polyimide resins could be autoclave processed within the goal fabrication parameters of the program [i.e., $\leq 505^{\circ}\text{K}$ (450°F) cure temperature and $\leq 1.4 \text{ MN/m}^2$ (200 psi) cure pressure]. The processing procedures developed for the PDA resins provided good fiber collimation and wetting utilizing Hercules A-S graphite fiber tows. During this work, a tersolvent mixture was identified for use as the laminating solvent. The solvent system was shown to expedite prepreg manufacture and the resultant composites were found to possess very promising mechanical properties. During work on this task, the non-destructive test (NDT) method of ultrasonic "C"-scan was used as a test procedure to assess the quality of composites produced. A detailed discussion of these activities is provided below.

3.1 INITIAL COMPOSITE SCREENING STUDIES

The initial composite fabrication studies were conducted to reproduce preliminary data obtained in Contract NAS3-15834 on prepreps prepared from type A-S fiber and the BFBI/BMPM resin employing DMF as the laminating solvent. Experimental studies then were conducted using NMP as the laminating solvent in place of DMF. Finally, the new BMPE containing PDA resin was evaluated as a resin matrix for graphite reinforced composites. During much of this work, ultrasonic "C"-scan was used as a test method to assess the quality of the composites prepared by conventional molding procedures (i.e., 0.7 MN/m^2 positive pressure and vacuum bag lay-up).

3.1.1 Initial Prepreg Manufacture

Prepreg tapes were prepared by drum winding at 8 tows per inch, Hercules A-S continuous graphite fiber impregnated with BFBA/BMPM amide acid solutions (BFBA is used when the amide acid of BFBI is employed). The fiber impregnation was performed in a resin bath containing 26-30% w/w resin solids solutions of the amide acid BFBA/BMPM mixture in either DMF or NMP. The tapes

then were air-dried for 1-6 days at room temperature, removed from the drum winder and subjected to additional "B"-stage cycles. The physical properties of tapes were determined using procedures described in Appendix D.

3.1.2 Initial Composite Fabrication

Composites were molded from the resultant graphite tape by first vacuum bagging the stacked prepreg [9 plies 7.6 cm by 10.2 cm (3-inch by 4-inch)] and then autoclave molding using various curing cycles in conjunction with positive pressure (see Figure 4 for schematic of vacuum bag lap-up). Three panels were fabricated using BFBA/BMPM resin and DMF as the solvent and then subjected to "C"-scan NDT testing to determine whether this process would yield the panel quality desired (i.e., <2% voids) prior to physical and/or mechanical testing. Initial "C"-scan studies (see Section 3.1.5) indicated that these composites possessed voids and in order to determine the quality of composites quantitatively, one panel was machined and tested (see Table VII). As the results clearly show, this panel contained a relatively high void content (i.e., ca. 4.0% v/v) which also was confirmed by photomicrographic inspection of a cross-section of the panel. At this early stage in the Task II studies, it was mutually agreed between TRW and the NASA Program Manager that the use of DMF as the laminating solvent should be discontinued because of its possible deleterious effects on mechanical properties of the composites. Consequently, N-methylpyrrolidone (NMP) was evaluated as a laminating solvent as discussed below.

3.1.3 Evaluation of NMP as the Laminating Solvent

Graphite tape was manufactured using NMP resin solutions in an analogous fashion to the DMF resin solutions. The graphite was impregnated in a resin bath containing 26-30% w/w of the BFBA/BMPM amide acid.

The resultant prepreg then was dried for 6 days on the winding drum. The first four days of drying was at room temperature and the last two days was under heat lamps [temperature approximately 322°K (130°F)]. This long drying cycle on the drum was required in order to lower the solvent content to a level where the prepreg tape could be handled. A solvent evolution study then was conducted at 394°K (250°F) and 405°K (270°F) for various times. After removal of the test samples from the "B"-staging oven, volatile

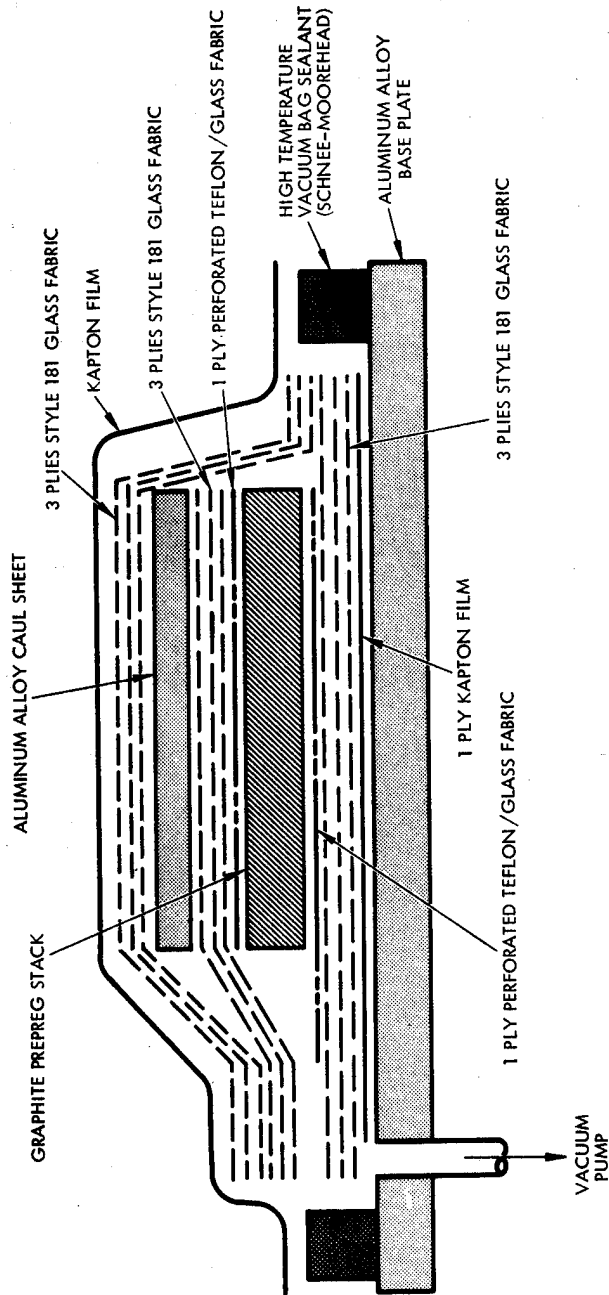


Figure 4. Schematic of Vacuum Bag Lay-Up

TABLE VII
PROPERTIES OF PRELIMINARY PANEL
EMPLOYING DMF AS THE LAMINATING SOLVENT

Property	Value
Density, g/cc	1.55
Resin Content, % w/w	25.7
Fiber Volume, % v/v	65.3
Void Volume, % v/v	3.9
Short Beam Shear ₂ Strength, MN/m ² (PSI)	51.3 (7300)

matter content was determined by testing samples at 561°K (550°F) for 30 minutes (see Table VIII). These data indicated that even at relatively high temperatures for solvent evaporation, the amount of volatile matter remaining was higher than desirable for subsequent processing operations.

TABLE VIII
SOLVENT REMOVAL STUDY USING NMP SOLVENT CONTAINING GRAPHITE TAPE

Testing Time (Hours)	Testing Temperature °K(°F)	
	394(250)	405(270)
0	24.1 ^a	24.1
1/2	19.0	15.7
1	15.9	13.6
2	14.7	11.1
3	13.2	10.4
4	11.4	9.8
5	11.3	-
6	11.3	9.1
7	-	8.7
24	-	7.5

a - percent volatile matter w/w

The prepregs prepared from the NMP resin varnish then were used for composite fabrication studies. Various "B"-staging, process and postcure cycles were screened by autoclave molding of panels. However, all of the panels (with one exception) contained various quantities and sizes of blisters and/or void areas. The one panel that looked acceptable by visual inspection was tested for mechanical and physical properties (see Table IX).

TABLE IX
PROPERTIES OF PANEL USING NMP AS THE LAMINATING SOLVENT

Property	Value
Flexural Strength, MN/m ² (KSI)	
at R.T.	1860 (265)
at 561°K (550°F)	530 (76)
Short Beam Shear Strength MN/m ² , (PSI) at 295°K	49.9 (7100)
Density, g/cc	1.54
Resin Content, % w/w	27.4
Void Volume, % v/v	4.0
Fiber Volume, % v/v	64

The low 561°K (550°F) strength retention together with the severe blistering of the panels, clearly indicated that residual NMP remained in the resin matrix after the cure cycle. Based on these results it was concluded that an alternative solvent or solvent mixture was required to process the PDA derived resins. The successful development of a tersolvent system for this resin system is described in Section 3.2.

3.1.4 Evaluation of BMPE Containing PDA Resin

The results obtained in Task I resin modification studies showed that the BMPE containing PDA resin was a potential candidate to be evaluated as a resin matrix in a graphite reinforced composite. To give a direct comparison of this new resin to the BFBI/BMPM resin, a BFBI/BMPM resin containing composite also was simultaneously prepared. For this screening study,

DMF was used as the laminating solvent to prepare the prepregs because NMP was found to be unacceptable as was discussed above.

Graphite tapes were manufactured using BFBI/BMPM and BFBI/90 BMPM: 10 BMPE amide acid by the procedure described in Section 3.1.1. The composites were fabricated, cured and postcured as reported in Section 3.1.2. The physical and mechanical properties of the tapes and composites were determined by procedures detailed in Appendix D. The results of this study are given in Table X. It was obvious that the BMPE containing PDA resin did not result in a significant increase in mechanical properties of the composite. Consequently, the approach was not pursued further.

3.1.5 Initial Evaluation of Ultrasonic "C" Scan Testing

The first tests of the "C"-scan technique were performed on the three composite samples prepared in Section 3.1.2. The "C"-scans were performed using Automation Industries Research System equipment employing the pulse echo technique. The test conditions included 2.25 MHz, sending crystal 0.23 cm SIL type, focus at reflector, 7.72 cm gate signal at typically good areas, 0 to 2.54 cm gate signal at suspect areas.

The same series of panels also were tested at the TRW Equipment Laboratories using the through transmittance technique. These tests were performed to compare the results of the pulse echo technique to the through transmittance technique. The testing parameters of this technique utilized a 10 MHz frequency, sending crystal 0.23 cm SIL type, receiving crystal 1.27 cm SIZ type, 50% screen height.

The "C"-scans (pulse echo) of the three panels are shown in Figure 5. By physical measurement methods, it was determined that panel 58-1 possessed a 3.9% v/v void content. The panel also was subjected to photomicrographic examination to confirm the presence of the void areas as determined by the "C"-scan technique. The photomicrograph (Figure 6) clearly shows void areas present in the composite.

TABLE X.
SUMMARY OF RESULTS OF COMPARATIVE
STUDY OF BMPE CONTAINING LAMINATING RESIN

Properties	Panel Number and Prepreg Drying Cycle Hr/°K (Hr/°F)	
	61 ^a 1/338 (1/150) 16/416 (16/290)	62 ^a 1/338 (1/150) 16/383 (16/230)
<u>Prepreg Properties</u>		
Volatiles Content, % w/w	2.9	-
Wet Resin Solids, % w/w	41.0	39.7
Dry Resin Solids, % w/w	37.4	32.8
<u>Flexural Strength, MN/m² (KSI)</u>		
at 295°K (RT)	1850 (263)	1790 (255)
at 561°K (550°F)	1570 (224)	1640 (233)
<u>Shear Strength, MN/m² (PSI)</u>		
at 295°K	49.4 (7020)	42.9 (6100)
<u>Physical Properties</u>		
Density, g/cc	1.56	1.55
Resin Content, % w/w	26.4	22.9
Void Content, % v/v	3.2	4.8
Fiber Volume, % v/v	65	68

a - Cure vacuum bag lay-up with heat up rate to 433°K (320°F) of 2-4°K/min (5-7°F/min); hold 30 minutes then apply 0.7 MN/m² (100 psi) positive pressure and heat to 478°K (400°F) at 2-4°K/min (5-7°F/min) rate; hold 2 hours, then cool under vacuum pressure to 294°K (70°F). Postcure composite under caul plate 30 minutes at 478°K (400°F), 60 minutes at 505°K (450°F), 533°K (500°F), 561°K (550°F) and 4 hours 589°K (600°F).

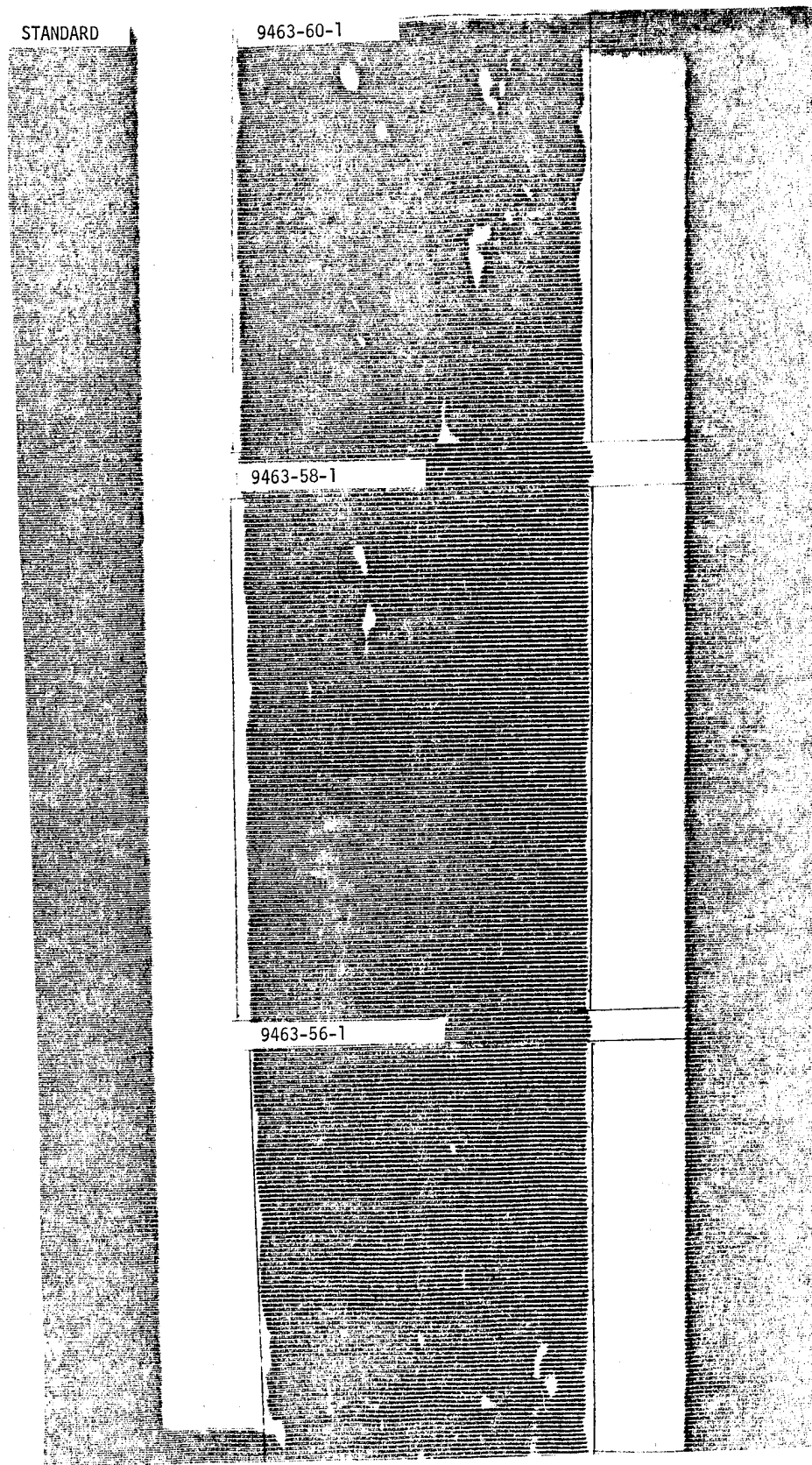


Figure 5. Ultrasonic "C" Scan of Graphite Fiber Composites
(Black Areas Are Good)

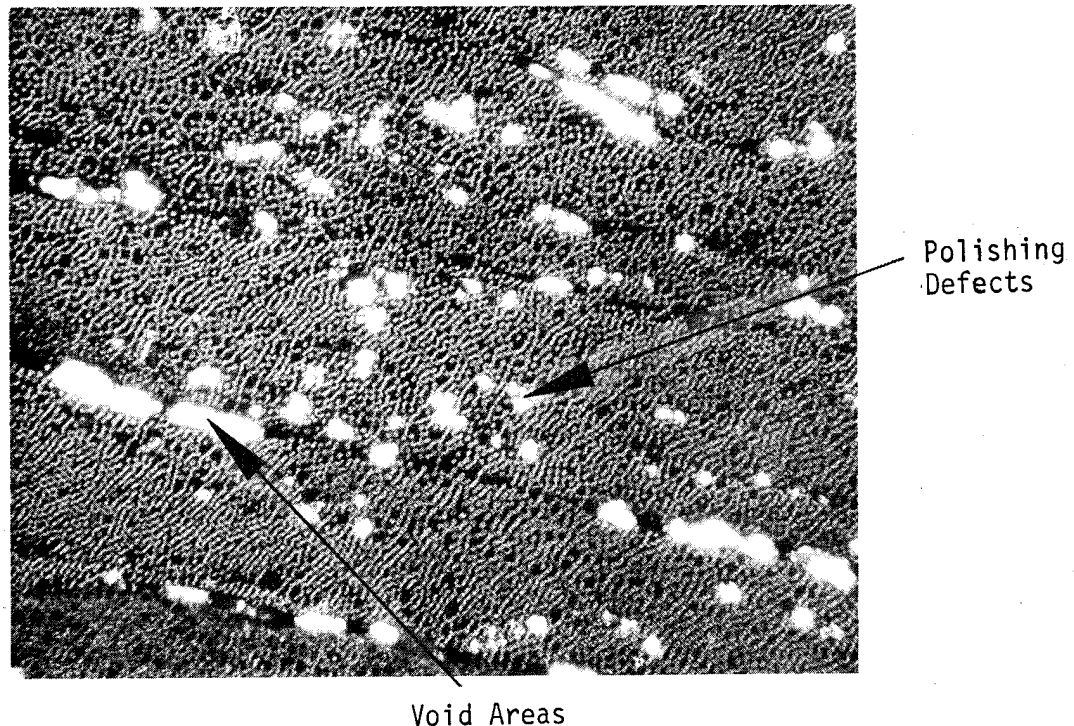


Figure 6. Photomicrograph of Panel 58-1
(110 Magnification)

3.2 ALTERNATIVE LAMINATING SOLVENTS

The results obtained during composite fabrication using NMP as the laminating solvent (see Section 3.1.2) indicated there were a number of inherent problems with this solvent. Some of the problems encountered with NMP were:

- Extended time required for solvent removal during prepreg preparation
- High temperatures required in "B"-stage to remove solvent
- Loss of elevated temperature composite properties

With these obvious shortcomings of NMP, studies then were initiated to find an alternative laminating solvent for the PDA resin. The results of this investigation are presented in the following sections.

3.2.1 Initial Solvent Selection

A screening study of potential solvents was first conducted for both the BFBA and BMPM components of the PDA monomer mixture. It was determined that BFBA (BFBI amide acid) is very soluble (>50% w/w) in methanol. However, BMPM is only sparingly soluble (<5% w/w) in this solvent. Thus the solvent screening study was concentrated on finding a suitable solvent for BMPM.

The possible candidate solvents identified for BMPM included acetone, chloroform, pyridine and butyrolactone. Of these solvents, acetone was selected as being the best candidate. Various mixtures of methanol and acetone then were prepared and the BFBA/BMPM resin was added to give a 30% (w/w) solids mixture. However, none of the solvent combinations yielded a homogenous solution. The insoluble portion in the mixtures was found to be BMPM.

Upon the suggestion of the NASA Project Manager, dioxane then was evaluated as a possible solvent. It was found that BMPM was sufficiently soluble (>20% w/w) in this solvent to make it a good candidate. However, the BFBA portion of the resin mixture was found to be insoluble in dioxane. Fortunately, by adding methanol to the dioxane/resin mixture a solution of 30% (w/w) solids was obtained.

To reduce the amount of higher boiling dioxane to a minimum in the solvent mixture, the possibility of adding acetone in its place was evaluated. A 30% w/w solids varnish was obtained in a solvent mixture consisting of 2:2:1 (by weight) of methanol, acetone and dioxane, respectively. The test varnish was found to have a shelf life of 2 days before precipitation of the resin commenced. Increasing the dioxane component to give a 1:1:1 (by weight) solvent mixture yielded a varnish with shelf life of greater than 4 weeks. The 1:1:1 tersolvent system was then evaluated as a laminating solvent as described in the following sections.

3.2.2 Evaluation of Methanol/Acetone/Dioxane as the Laminating Solvent

Graphite tape manufacture and subsequent composite fabrication using a varnish of BFBA/BMPM in methanol/acetone/dioxane and A-S graphite then was initiated using the same prepregging procedure as described in Section 3.1.1. After only two hours of drying, the volatile content of the tape was in the range of 18-20% w/w when determined by procedures described in Appendix D. A graphite composite (panel number 93) then was fabricated using procedures described in Section 3.1.4.

The physical and mechanical properties for this panel then were determined (Table XI). The results showed that the mechanical properties were comparable to those obtained for this system using DMF as the laminating solvent. As a result, further studies were conducted employing the tersolvent approach to optimize the processing conditions and properties of the resultant composites.

TABLE XI.
SUMMARY RESULTS OF GRAPHITE COMPOSITES USING
METHANOL/ACETONE/DIOXANE AND ETHANOL/ACETONE/DIOXANE LAMINATING SOLVENTS

Properties	Panel Number and Prepreg Drying Cycle Hr/°K (Hr/°F)		
	93 ^a 1.5/338 (1.5/150) 2.0/394 (2.0/250)	94 ^a 1.0/338 (1.0/150) 3.0/394 (3.0/250)	95
<u>Flexural Strength, MN/m² (KSI)</u>			
at 295°K (RT)	1490 (212)	1580 (225)	1510(215)
at 561°K (550°F)	-	1030 (146)	980(140)
<u>Shear Strength, MN/m² (PSI)</u>			
at 295°K (RT)	54.8 (7800)	72.4 (10,300)	57.6 (8200)
<u>Physical Properties</u>			
Density, g/cc	1.54	1.58	1.58
Resin Content, % w/w	28.5	29.7	25.3
Void Content, % v/v	3.7	<1	2.5
Fiber Volume, % v/v	62.3	63.1	66.9

a - Cure same as cure cycle described in note on Table X

The first study investigated the potential use of ethanol as the alcohol portion of the tersolvent in place of methanol. Ethanol was selected for use in an attempt to decrease the rate of solvent evaporation and to improve prepreg handleability. The composite (panel 94) was fabricated using the same procedure as was used for panel 93. During prepreg manufacture, it was found that the varnish possessed a very limited self-life (ca. 1 hour). Consequently, only one panel was prepared using the ethanol/acetone/dioxane mixture. The physical and mechanical properties obtained for the panel are given in Table XI. The most significant results are the increased short beam shear strength (72.4 MN/m²) and the low void content. In an attempt to duplicate these results using methanol as the alcohol portion of the tersolvent, additional processing studies were performed as described below.

The graphite tape prepared from the BFBA/BMPM resin in the 1:1:1 methanol:acetone:dioxane solvent system was used without a preliminary drying cycle to increase its handelability (i.e., good drape and tack). The autoclave

cycle employed was the same as shown in Table X except for the following:

Only 50.8 kN/m^2 vacuum pressure was used during the 377°K (220°F) and 433°K (320°F) soak levels. After 433°K (330°F) soak level, $94.8\text{-}98.2 \text{ kN/m}^2$ vacuum and 0.7 MN/m^2 (100 psi) positive pressure was applied and the composite cured at 473°K (390°F) for two hours and then cooled to room temperature under vacuum pressure.

Physical and mechanical properties for the panel (panel 95) were determined (see Table XI). As the results indicate, the process provided a promising composite panel. The short beam shear was not as high as that obtained for the ethanol system, but the value represented a significant improvement over that observed for the DMF varnish.

Four additional panels were then prepared to study the effect of different cure cycles. The processing conditions used to fabricate the panels are given in Table XII. After the panels were removed from the autoclave, weight measurements and "C"-scan NDT examinations were performed on three of the panels.

The panels then were postcured in the same manner as for previous graphite composites [i.e., 30 minutes at 478°K (400°F), 60 minutes at 505°K (450°F), 533°K (500°F), 561°K (550°F), and 4 hours at 589°K (600°F)]. The panel weight losses were determined and additional "C"-scan NDT testing was performed. The physical and mechanical properties of the panels also were determined. Discussion of the results obtained from this processing study is given below.

The data presented in Table XII clearly showed that the methanol/acetone/dioxane solvent mixture provided composite panels possessing very promising properties. For example, panel 96-8 was found to have a R.T. short beam shear strength of 78.0 MN/m^2 (11.1 ksi) and a R.T. flexural strength of 1980 MN/m^2 (281 ksi). These values were the highest observed to date for this resin system. Because the vacuum was lost on panel 96-7, a full assessment of the different processing conditions could not be made at the conclusion of this study. However, a general set of processing conditions was formulated

TABLE XII
INITIAL RESULTS OF CURE STAGING STUDY USING
METHANOL/ACETONE/DIOXANE AS RESIN SOLVENT

Properties	Panel Number and Composite Cure Cycle			
	96-5	96-6 ⁽¹⁾	96-7 ⁽²⁾	96-8
A Stage Temp, °K(°F)	360(190)	400(260)	377(220)	360(190)
A Stage Time, Minutes	120	120	240	240
A Stage Vacuum, (mm Hg)	381	381	127	127
B Stage Temp, °K(°F)	438(330)	438(330)	438(330)	428(310)
B Stage Time, Minutes	30	30	30	60
B Stage Vacuum (mm Hg)	381	381	127	127
<u>C Stage</u>	(3)	(3)	(3)	(3)
Weight Loss During Post Cure (% w/w)	2.1	2.8	1.9	1.9
<u>Flexural Strength, MN/m² (KSI)</u>				
at 295°K (RT)	1800(256)	1080(154)	1650(235)	1980(281)
at 561°K (550°F)	880(125)	-	-	1140(162)
<u>Shear Strength, MN/m² (KSI)</u>				
at 295°K (RT)	59.8(8.5)	58.3(8.3)	-	78.0(11.1)
at 561°K (550°F)	35.2(5.0)	-	-	35.2(5.0)
Density, g/cc	1.58	1.57	1.57	1.60
Resin Content, % w/w	24.9	30.5	23.9	23.4
Void Content, % v/v	2.8	2.7	3.2	1.6
Fiber Content, % v/v	67.4	62.0	67.9	69.6

- (1) This panel blistered during postcure and only part of the panel was available for testing.
- (2) Lost vacuum during "C"-stage cure and only acceptable parts of panel were tested.
- (3) Full vacuum (i.e., 94.8-98.2 kN/m² vacuum) and 0.7 MN/m² positive pressure was applied and the part cured 120 minutes at 473°K (390°F).
- (4) Results obtained on "Cal-Tester" apparatus, values are average of five specimens.

which included the following:

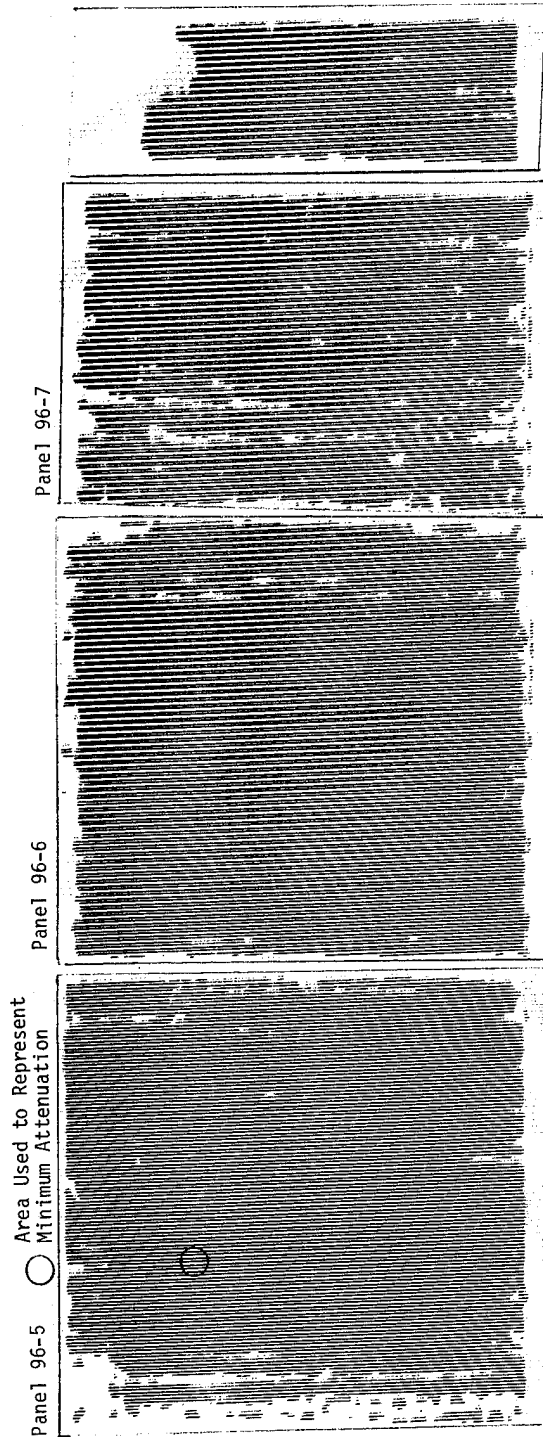
- A stage temperature, 360°K
- A stage time, 240 minutes
- B stage temperature 438°K
- B stage time, 60 minutes
- Cure temperature, 473°K

The "C"-scan results on the cured and postcured panels were used to determine the stage in the processing cycle that void formation occurred (i.e., either during the cure cycle or postcure cycle). The scans obtained for the cured panels (Figure 7) showed that the composites varied considerably in the amount of suspect areas. It was also evident that for the cured panels and postcured panels, the suspect areas were concentrated on the edges of the panels. Comparison of "C"-scans (Figures 7 and 8) of the cured and postcured panels clearly indicated that a considerable change in the composites had occurred. In fact, the physical change was so significant that new instrument settings were required to obtain the same signal height ratio so that a direct comparison could be made between the cured and postcured panels.

Three specimens from panel 96-5 were subjected to micrographic examination to confirm the "C"-scan results that the suspect area were indeed void areas. The location of each specimen taken from panel 96-5 is given in Figure 9. The photomicrographs (Figures 10 through 12) were taken using polarized light to show the void areas more clearly. Based on the results of the "C"-scan analysis mechanical tests and photomicrographs, the following conclusions were drawn:

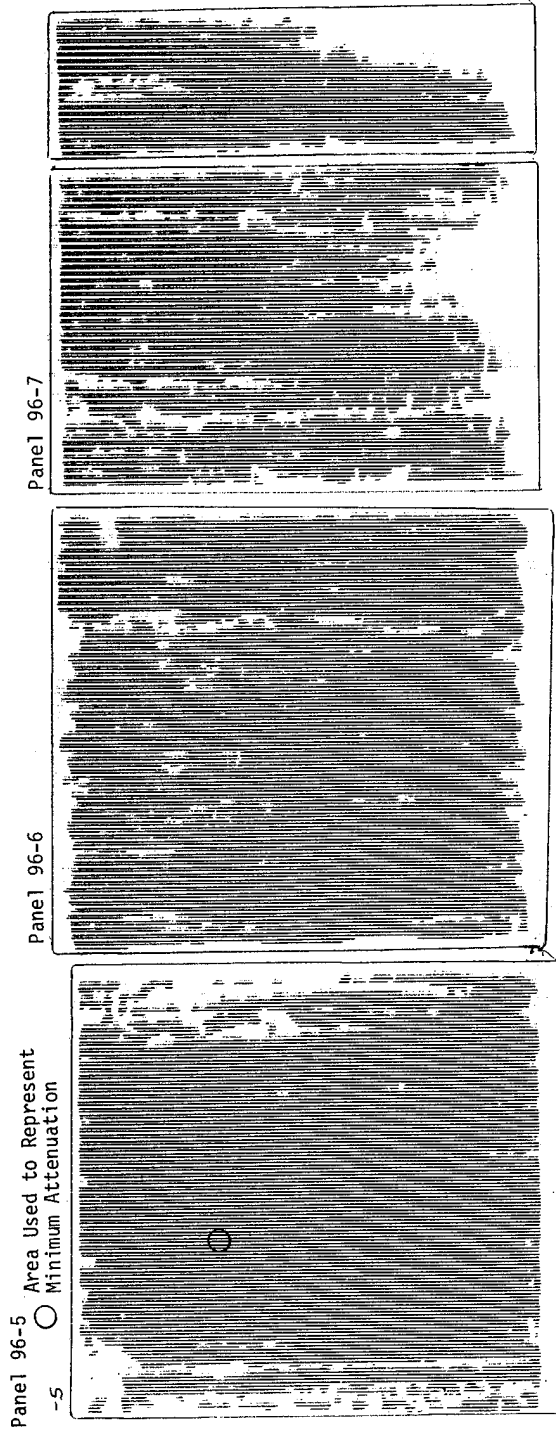
- Low void content composite panels can be obtained by the selected autoclave molding process, however,
- Significant void formation occurs during the postcure cycle evaluated during the reported screening studies.

The research efforts of Task II studies then were directed toward defining a new postcure cycle for the composites as described below.



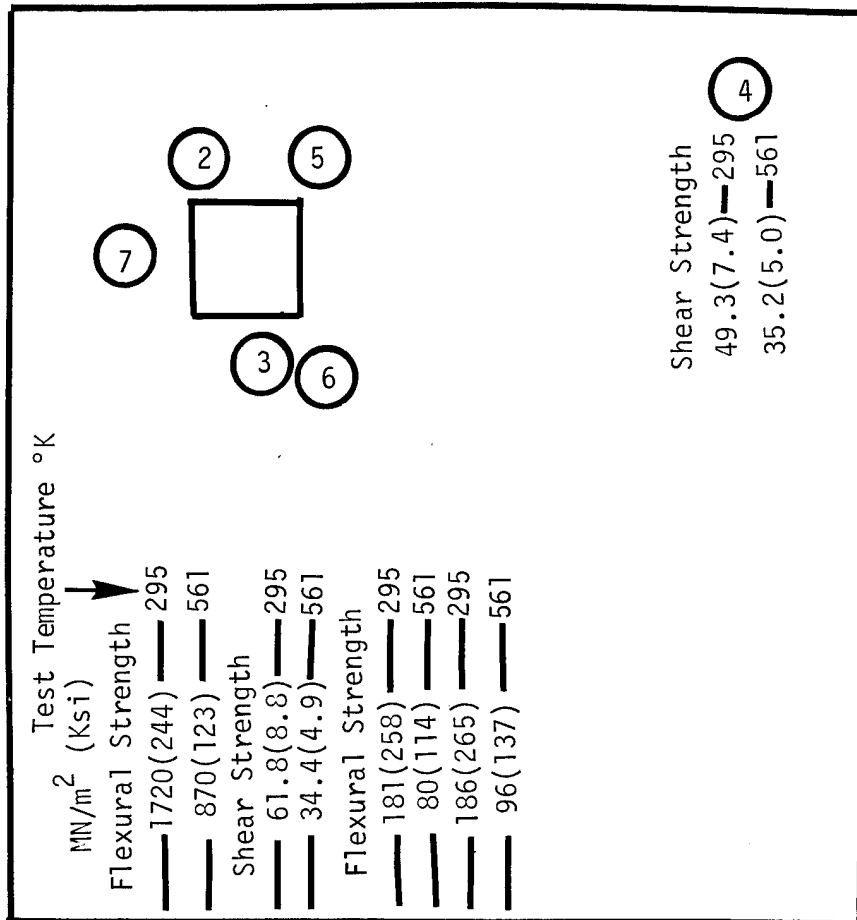
5.0 MHz
Back Reflection
Focus at Top of Part

Figure 7. Ultrasonic "C" Scans of Cured Graphite Composites Before Postcure



5.0 MHZ
Back Reflection
Focus at Top of Part

Figure 8. Ultrasonic "C" Scans of Postcured Graphite Composites.



NOTE: Samples 2, 3 and 4 were photomicrographs (see Figures 10 through 12).
Samples 5, 6 and 7 were for Density and Resin Content.

Sample	Density, g/cc	Resin Content, % w/w	Void Volume, % v/v
5	1.57	25.7	2.7
6	1.58	23.9	2.6
7	1.57	24.4	3.1

Figure 9. Specimen Location on Panel 96-5.



Figure 10. Photomicrograph of Specimen 2 From Panel 96-5. (110X, Polarized Light)



Figure 11. Photomicrograph of Specimen 3 From Panel 96-5. (110X, Polarized Light)

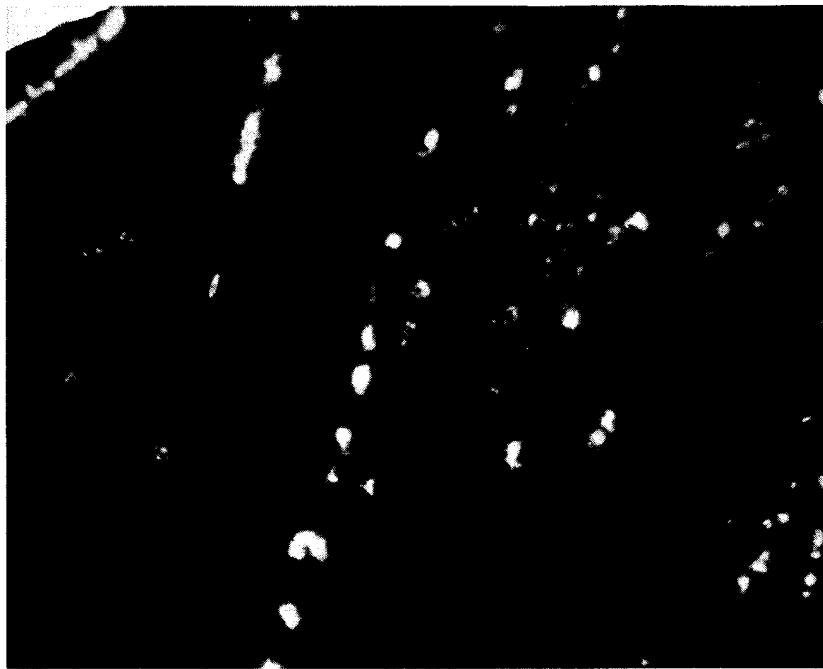


Figure 12. Photomicrograph of Specimen 4 From Panel 96-5. (110X, Polarized Light)

3.2.3 Preliminary Postcure Studies

As was discussed above, it was evident that void formation was occurring during the postcure cycle. Consequently, an investigation into postcure conditions was conducted. A BFBA/BMPM graphite composite was fabricated using the following procedure:

The graphite prepreg was prepared from a BFBA/BMPM tersolvent varnish and vacuum bagged and introduced into the autoclave. The initial vacuum bag pressure was set at 50.8 kN/m^2 and the assembly was heated to 377°K (220°F) and held for 2 hours. The assembly then was heated to 433°K (320°F) and held for 30 minutes. Full vacuum bag pressure (i.e., $94.8\text{-}98.2 \text{ kN/m}^2$) and 0.7 MN/m^2 cure pressure then were applied and the assembly was heated to 473°K (390°F) for two hours and then cooled to room temperature under vacuum bag pressure. The postcure cycle included 1 hour each at 478°K (400°F), 490°K (425°F), 505°K (450°F), 518°K (475°F), 533°K (500°F), 546°K (525°F), then 16 hours at 561°K (550°F), and finally 4 hours at 589°K (600°F).

The significant change in the postcure cycle was extending the time at 550°F . The resultant composite's mechanical and physical properties then were determined and are reported in Table XIII. Along with the physical and mechanical property determination, "C"-scan NDT testing (see Figure 13) and micro inspection (see Figure 14) also were obtained. Specimen location for the above testing is shown in Figure 15.

The data obtained for this panel clearly indicated that an extended postcure resulted in improved physical and mechanical properties. For example, the void content was <2% v/v and the short beam shear value was 71.7 MN/m² at R.T. The "C"-scan indicated that even after postcure the panel was defect free. Based on these results additional postcure studies were performed in Task III studies.

It was concluded from the work that the BFBA/BMPM resin showed high promise of producing outstanding reinforced composites when processed using the tersolvent varnish and the extended postcure cycle. Additional refinements in the processing cycle were examined in Task III studies.

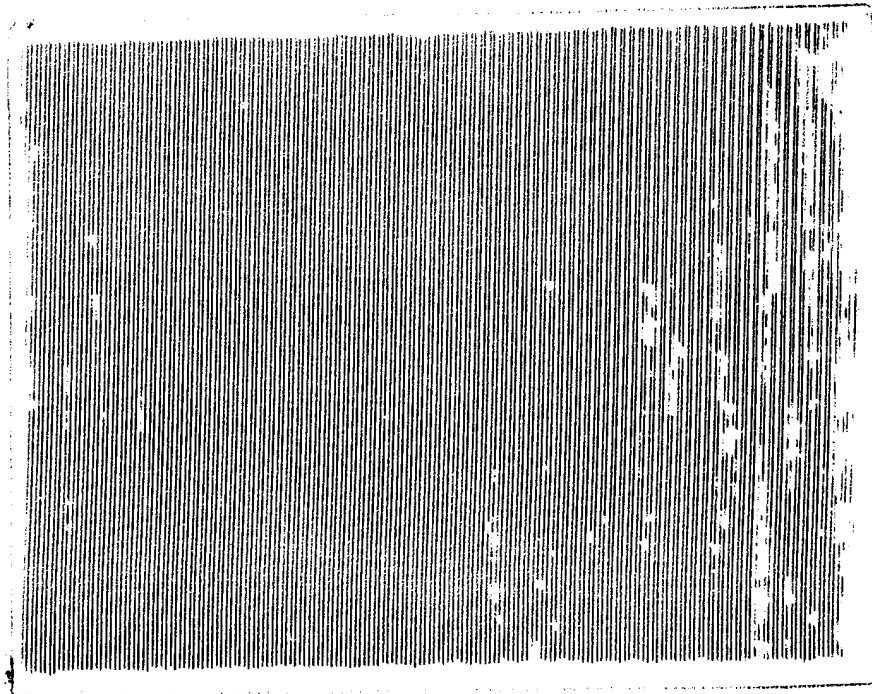
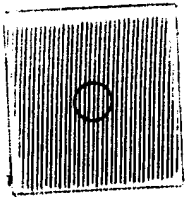
TABLE XIII.
PROPERTIES OF COMPOSITE USING AN EXTENDED POSTCURE CYCLE
(PANEL 99-2)

Property	Value
<u>Composite Weight Loss</u>	
During Autoclave Cycle, % w/w	39.7
During Postcure Cycle, % w/w	1.4
<u>Flexural Strength, MN/m² (KSI)^(a)</u>	
at 295 K (RT)	2220 (314)
at 561 K (550°F)	1603 (228)
<u>Shear Strength, MN/m² (PSI)^(a)</u>	
at 295 K (RT)	71.7 (10.2)
at 561 K (550°F)	38.7 (5.5)
<u>Physical Properties</u>	
Density, g/cc	1.58
Resin Content, % w/w	26.3
Void Volume, % v/v	1.9
Fiber Volume, % v/v	66.2

(a) Results obtained on "Cal-Tester" apparatus, values are average of four specimens.

9463-99-2B

Area to
Represent
Minimum
Attenuation



5.0 MHz
Back Reflection
Focus at Top of Part

Figure 13. C-scan of Panel 99-2

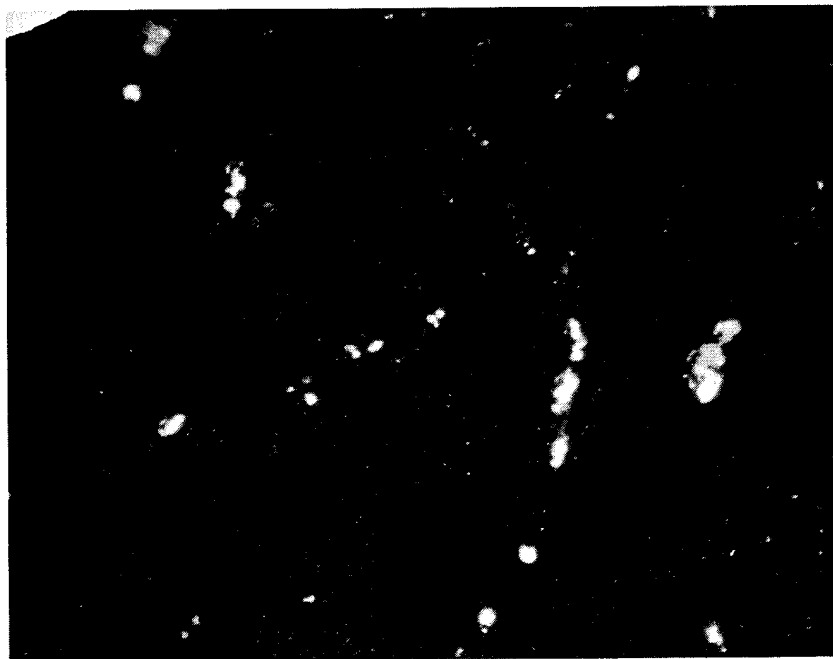
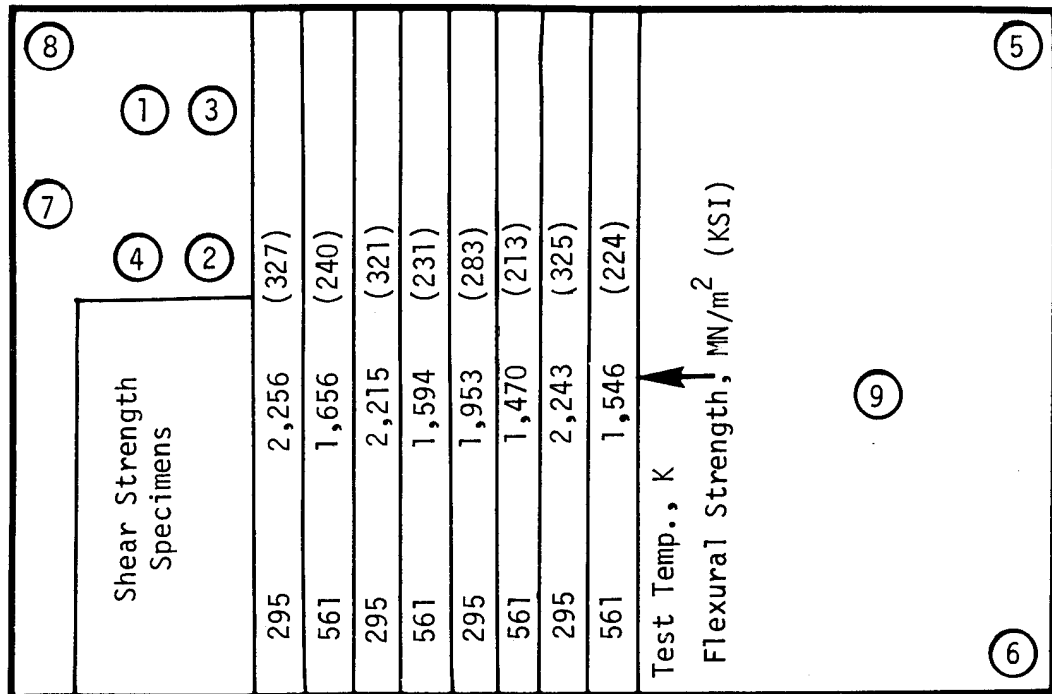


Figure 14. Photomicrograph of Panel 99-2
(110X Polarized Light)



Specimen Numbers 1, 2 used for photomicrographs.

Specimen Numbers 3, 4, 5, 6, 7, 8, 9 used for specific gravity and resin content.

Sample	Density (g/cc)	Resin Content (% w/w)	Void Volume (% v/v)
3	1.62	25.5	< 1
4	1.61	25.2	< 1
5	1.54	29.4	2.5
6	1.53	32.3	3.1
7	1.59	26.4	2.4
8	1.57	26.1	1.4
9	1.57	28.4	1.8

Figure 15. Specimen Location on Panel 99-2.

IV. TASK III - REPRODUCIBILITY STUDIES

The objective of this task was to investigate potential improvements of the resin and process employing the new tersolvent so that reproducible composite panels were produced. The criteria used to assess the reproducibility were high mechanical properties and low (<2%) void contents. It was shown in these studies that the postcure cycle and the purity of the BMPM ingredient are critical to obtain reasonably reproducible composites. Additionally, it was determined that some change of the BFBA/BMPM varnish in the tersolvent does occur with time. The details of these studies are presented in the following sections.

4.1 CURE AND POSTCURE STUDIES

Based on the results obtained at the end of Task II studies showing that an extended postcure cycle produced lower void content panels, a cure/postcure screening matrix was performed as part of Task III studies in which the effect of duration of postcure at various temperatures was investigated. The matrix investigated is shown in Figure 16. The processing conditions of the graphite tape and composites were as described in Section 3.2.3, except the dwell times used at 473°K (390°F) are as depicted in Figure 16. After postcure, the panels were allowed to cool to ambient conditions and visual examination of the composites indicated a high degree of blistering had occurred. Physical and mechanical properties could be obtained only on panel 100-1 and only final weight loss values during postcure were determined for panels 100-2, 100-3 and 100-4 (see Table XIV). At this point, the blistering was attributed to changes in the processing cycle. Therefore, another series of composites was fabricated using the identical initial cycle described in Section 3.2.3 to assess panel to panel reproducibility, except that two of the cured composites were postcured for 24 hours at 589°K (600°F) instead of the previous 4 hours for comparative purposes. A few small blisters occurred on one of the panels postcured 24 hours at 589°K (600°F), but the other two appeared to be visually acceptable. Mechanical and physical properties were determined and are presented in Table XV.

Panel Number	Initial Cure Time ^a At 473°K (390°F) (Hours)	Postcure Time Hours	Postcure Temp. °K (°F)
100-1	8	8	505 (450)
		8	533 (500)
		16	561 (550)
		4	589 (600)
100-2	16	4	505 (450)
		4	533 (500)
		16	561 (550)
		4	589 (600)
100-3	8	8	505 (450)
		8	533 (500)
		16	561 (550)
		4	589 (600)
100-4	16	4	505 (450)
		4	533 (500)
		16	561 (550)
		4	589 (600)

^aDwell time.

Figure 16. Cure/Postcure Test Matrix

TABLE XIV.
PROPERTIES OF COMPOSITES FROM CURE/POSTCURE STUDY

Property	Composite Panel Number			
	100-1	100-2	100-3	100-4
<u>Flexural Stress MN/m² (KSI) (a)</u>				
at 245°K (RT)	2110 (284)	(c)	(c)	(c)
at 561°K (550°F)	1340 (190)	(c)	(c)	(c)
<u>Short Beam Shear Stress MN/m² (PSI)</u>				
at 295°K (RT)	60.1 (8.6)	(c)	(c)	(c)
at 561°K (550°F)	44.3 (6.3)	(c)	(c)	(c)
<u>Physical Properties</u>				
Composite Weight Loss, % w/w ^(b)	1.8	3.1	2.5	3.0
Density, g/cc	1.49	(c)	(c)	(c)
Resin Content, % w/w	22.5	(c)	(c)	(c)
Void Volume, % v/v	8.6	(c)	(c)	(c)
Fiber Volume, % v/v	56	(c)	(c)	(c)

(a) Results obtained on "Cal Tester" apparatus, values are averages of five specimens.

(b) Weight loss of composite during postcure cycle.

(c) Panel not tested due to blistering on postcure.

TABLE XV.
PROPERTIES OF GRAPHITE COMPOSITES

Property	Composite Panel Number		
	101-1 ^(c)	101-2	101-3 ^(c)
Flexural Strength MN/m ² (KSI) ^(a)			
at 295°K (RT)	1860 (265)	1800 (256)	1810 (258)
at 561°K (550°F)	1290 (184)	1300 (185)	1190 (169)
Shear Strength MN/m ² (PSI) ^(a)			
at 295°K (RT)	63.3 (9.0)	76.6 (10.9)	81.5 (11.6)
at 561°K (550°F)	47.1 (6.7)	54.1 (7.7)	43.4 (6.2)
Physical Properties			
Composite Weight Loss, % w/w ^(b)	3.6	3.6	3.2
Resin Content, % w/w	25.5	23.7	27.2
Void Volume, % v/v	7.1	7.0	2.8
Fiber Volume, % v/v	63.5	65.5	64.5
Density, g/cc	1.50	1.51	1.56
Postcure Time @ 589°K (600°F) ^(b)	24	24	4

(a) Results obtained on "Cal-Tester" apparatus, values are average of three specimens.

(b) Weight loss of composite during postcure cycle.

(c) Panel possessed a few small blisters.

Inspection of the results presented in Table XV showed several interesting trends when compared with the results of the first panel prepared using the extended postcure cycle as presented in Table XIII.

- The flexural strengths of the triplicate panels are lower, both at 295°K (R.T.) and 561°K (550°F).
- The shear strength retention at 561°K is consistently higher than that given in Table XIII.
- The composite weight losses on postcure and void volumes are all higher than those given in Table XIII.

These results all strongly indicated that the resin samples used in the two composite fabrication attempts differed in some manner, because all other process variables were fixed. This difference is particularly evident in view of the greater than 100% increase in void volume and

composite weight loss on postcure. Consequently, studies were conducted to assess the effect of aging on the BFBA/BMPM varnish and to set quality standards on the ingredients used in the varnish.

4.2 VARNISH STUDIES

It was evident from the results obtained above that the resin or resin varnish used to prepare the above series of panels was the cause of the reproducibility problems. As a result, the first study conducted investigated the effect of aging on the varnish. Then a series of composites was prepared using the aged varnish solutions. During these composite fabrication studies, the source of the blistering problem was discovered. The details are given below.

4.2.1 Varnish Aging Studies

Samples of a resin varnish (30% w/w solids in 1:1:1 by weight methanol:acetone:dioxane) were prepared by the usual procedure and then stored in sealed containers. Samples of each varnish then were tested

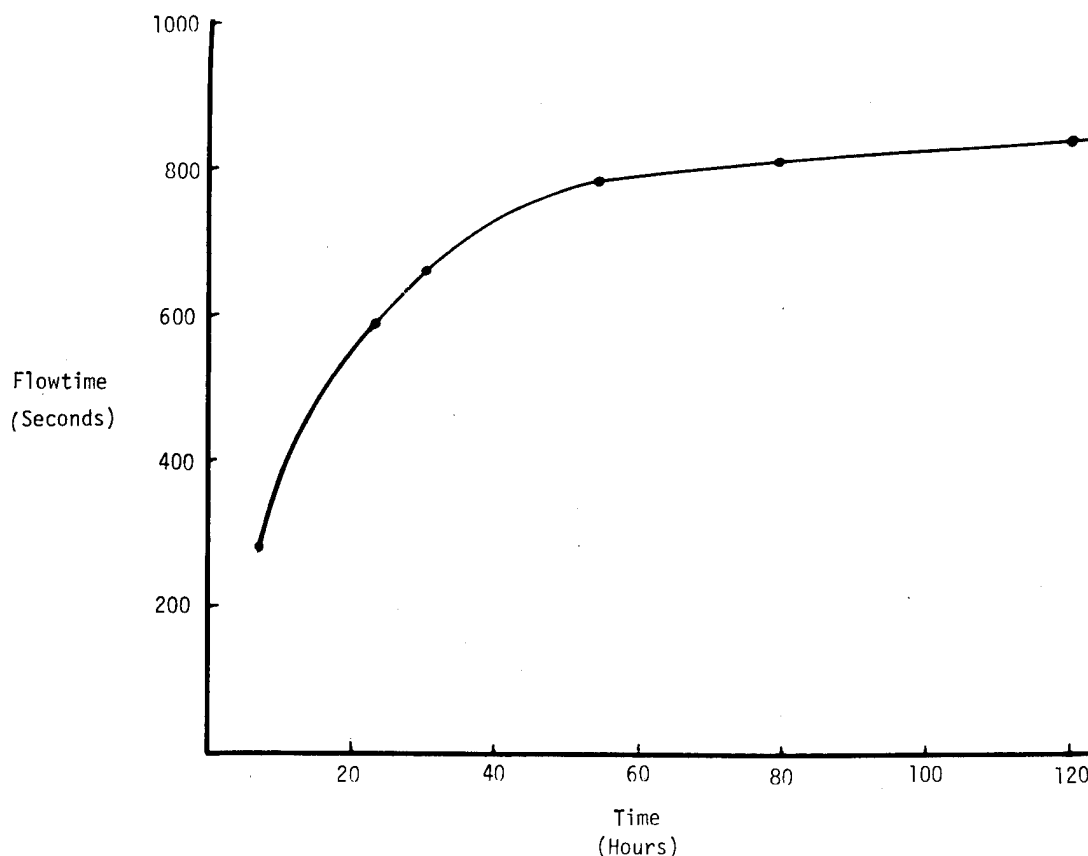


Figure 17. Results of Varnish Aging Study

periodically by measuring the flow times in an Ostwald viscometer. The results obtained from this study are displayed graphically in Figure 17. It was evident that a chemical or physical change did take place in the varnish with time. As can be seen in Figure 17, the viscosity of the varnish stabilized after ~50 hours. Similar results were obtained using a Brookfield viscometer later in the program. Consequently, it was concluded that the PDA varnish should be aged for a minimum of 48 hours before being used to prepare prepregs. An aged varnish was used to prepare a composite as discussed in the next section.

4.2.2 Composite Studies With Aged Varnish

A varnish which had been aged for 48 hours was used to prepare graphite prepreg in the usual fashion. A BFBA/BMPM graphite composite was fabricated using the following processing cycle.

The graphite prepreg was vacuum bagged as previously described and introduced into the autoclave. The initial vacuum bag pressure was set at 50.8 kN/m^2 and the assembly was heated to 377°K (220°F) and held for 2 hours. The assembly then was heated to 433°K (320°F) and held for 30 minutes. Full vacuum bag pressure (i.e., $94.8\text{-}98.2 \text{ kN/m}^2$) and 0.7 MN/m^2 cure pressure then were applied and the assembly was heated to 473°K (390°F) for two hours and then cooled to room temperature under vacuum bag pressure. The postcure cycle included 1 hour each of 478°K (400°F), 490°K (425°F), 505°K (450°F), 518°K (475°F), 533°K (500°F), 546°K (525°F), then 16 hours at 561°K (550°F).

It was found that the composite was badly blistered after the post-cure cycle. The exact temperature at which the blistering occurred was not determined in this run because the panel was not inspected after each temperature increase. Consequently, another panel was prepared from a new batch of resin so that the temperature at which the blistering occurred could be determined. This time blistering was observed after the 490°K (425°F) treatment. It was very evident from these results that the observed blistering and void formation was caused by an impurity in the resin itself.

Consequently, infrared analysis of the monomers was conducted. It was found that some amide-acid was present in the BMPM that had been used to prepare the two panels discussed above. Analysis of other samples of BMPM on hand also revealed trace amounts of amide-acid present. Therefore, the BMPM monomer was purified further by recrystallization (twice from methanol) until no amide-acid band was detected in the infrared spectrum.

The purified BMPM then was used to prepare a laminating varnish in the usual fashion. However, during the 48-hour aging, a thick, sticky precipitate formed. This material was identified as BMPM giving indication that the purified BMPM was less soluble in the solvent than the impure monomer used previously. As a result, the dioxane ratio was increased to give a 4:3:3 (by weight) ratio of dioxane:acetone:methanol. The resulting varnish was aged for thirty hours at which time it had turned slightly cloudy. A composite was fabricated as described earlier and postcured with the same cycle as above except that the panel was heated to 589°K (600°F) for 4 hours. The resultant composite's mechanical and physical properties were determined in the usual fashion and are reported in Table XVI along with results from an acceptable panel (96-8) prepared early in Task II.

A second panel (8-2) also was fabricated in the same manner and its mechanical and physical properties were determined to be similar to those of sample 8-1 presented. Because both panels displayed properties similar to those obtained earlier in the program (see Table XVI), it was believed that the resin reproducibility problem had been solved. As a result, fabrication of large panels in Task IV studies was initiated. The panels were used for the detailed testing.

TABLE XVI.
COMPARISON OF PROPERTIES OF GRAPHITE COMPOSITES

Property	Composite Panel Number	
	8-1 ^a	96-8 ^a
<u>Flexural Strength MN/m² (Ksi)^a</u>		
at 295°K	1905 (271)	1980 (281)
at 550°K	1230 (175)	1140 (162)
<u>Shear Strength MN/m² (Ksi)</u>		
at 295°K	78.0 (11.1)	78.0 (11.1)
at 561°K	49.2 (7.0)	35.2 (5.0)
<u>Physical Properties</u>		
Composite Weight Loss, % w/w ^b	2.6	1.9
Resin Content, % w/w	22.6	23.4
Void Volume, % v/v	<1	1.6
Fiber Volume, % v/v	72	69.6
Density, g/cc	1.64	1.60

^aResults obtained on "Cal-Tester" apparatus, values are average of three specimens.

^bWeight loss during postcure cycle.

V. TASK IV - DETAILED EVALUATION

Composite panels were autoclave molded containing PDA (BFBA/BMPM in acetone/methanol/dioxane solution) with Hercules A-S graphite fiber reinforcement using the procedures defined in Task III (see Section 4.2.2). However, it should be noted that the processing conditions of the PDA were not optimized. This fact is readily apparent by the wide scatter of flexural and shear properties of the composites (See Table XVII, panels 17 versus panels 20). Those panels possessing the higher mechanical properties and lowest void contents were used in the 561°K (550°F) isothermal aging tests and the remaining panels used in the 533°K (500°F) isothermal aging and water boil evaluations. Details of the work are provided below.

5.1 TEST PROCEDURES

The 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 0.02 cm and the short beam shear specimens were 0.6 cm by 1.2 cm by 0.02 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 m³/sec. Air temperature in the two ovens was stabilized at the aging temperature, i.e., 533°K (500°F) and 561°K (550°F). Specimens were withdrawn from the air circulating ovens after aging durations of 200, 400, 600 and 1000 hours and placed in a desiccator. Flexural and shear properties were determined on as-molded, after 2 hours water boil and isothermally aged specimens in accordance with the procedures defined in Appendix D. Weight loss calculations were made on the isothermally aged specimens and resin retention plots were made.

5.2 TEST RESULTS

Two separate sets of panels were used in the isothermal aging tests and another panel was used in determining the strength retention after specimens had been submerged in boiling water for two hours. The initial mechanical and physical properties of the panels used in the isothermal aging test are presented in Table XVII, the panel used in the water boil

TABLE XVII
SUMMARY PROPERTIES OF GRAPHITE COMPOSITES USED FOR ISOTHERMAL AGING

Composite Physical Properties				Composite Mechanical Properties				Panel Number (6)
Resin Content % w/w	Specific Gravity g/cc (1)	Void Volume % v/v (2)	Fiber Volume % v/v (3)	Flexural Strength MN/m ² (KSI) (4)	Shortbeam Shear Strength MN/m ² (KSI) (5)	Flexural Modulus GN/m ² (MSI)	Test Temperature °K	
28.3	1.67	>1	68.0	1819 (264)	102.0 (14.8)	123 (17.9)	295	17-1
23.1	1.66	>1	72.5	903 (131)	42.7 (6.2)	114 (16.6)	561	17-2
20.2	1.62	1.4	73.5	1764 (256)	67.5 (9.8)	120 (17.4)		20-1
24.0	1.56	3.8	67.4	1310 (190)	48.9 (7.1)	120 (17.4)		20-2

(1) Specific gravity determined with following formula:

$$\frac{\text{Specimen Weight in Air}}{\text{Specimen Weight in Air} - \text{Specimen Weight in H}_2\text{O}}$$

- (2) Calculated from resin contents and measured specific gravity values
- (3) Calculated from resin content value
- (4) The test span was determined by multiplying the specimen thickness by 32
- (5) The specimen length was six times specimen thickness and test span was four times specimen thickness
- (6) The composite mechanical properties were determined by the use of specimens from both composites, whereas physical properties were determined on each separate composite

tests, Table XVIII, and the mechanical properties of the specimens after isothermal aging, Table XIX. The initial properties of the unaged and two hour water boil PDA/A-S graphite composite specimens were comparable to the state-of-the-art polyimide resin systems, 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 18 and 19. Corresponding properties retention data also were obtained after isothermal aging for 1000 hours at 533°K and 561°K (see Figures 20 through 23). These results were interpreted to mean that the PDA resin is suitable for processing under mild conditions [i.e., 437°K (390°F) cure temperature and 0.7 MN/m^2 (100 psig) molding pressure].

However, after 1000-hour aging duration at 561°K , the PDA composites demonstrated a significantly higher degradation rate than similar PDA composites using HMS graphite previously studied (Reference 1). This additional weight loss could most probably be attributed to both the relatively low initial resin content of the composites and/or degradation of the A-S graphite fiber. Therefore, further experimental work is necessary in order to:

- Optimize processing procedures so that precise resin content control in the cured composite is achieved and
- Evaluate the PDA resin with more thermally stable graphite fibers (e.g., HMS) so that a valid evaluation of the PDA resin's high temperature (561°K) performance can be assessed.

TABLE XVIII
SUMMARY WATER BOIL TEST

Composite Physical Properties				Composite Mechanical Properties			
Resin Content % w/w	Specific Gravity g/cc (1)	Void Volume % v/v (2)	Fiber Volume % v/v (3)	Flexural Strength MN/m ² (KSI) (4)	Shortbeam Shear Strength MN/m ² (KSI) (5)	Flexural Modulus GN/m ² (MSI)	Test Temperature °K
23.5	1.60	1.5	39.5	1426 (207)	64.1 (9.3)	117 (17.0)	295
				992 (144)	40.7 (5.9)	121 (17.5)	561
				1440 (209)	53.7 (7.8)	115 (16.7)	295 (6)
				950 (138)	39.3 (5.7)	113 (16.4)	561 (6)

(1) Specific gravity determined with following formula:

$$\frac{\text{Specimen Weight in Air}}{\text{Specimen Weight in H}_2\text{O}}$$

- (2) Calculated from resin content and measured specific gravity values
- (3) Calculated from resin content value
- (4) The test span was determined by multiplying the specimen thickness by 32
- (5) The specimen length was six times specimen thickness and test span was four times specimen thickness
- (6) Specimens conditioned two hours boiling H₂O prior to testing

TABLE XIX
ISOTHERMAL AGING PROPERTIES OF PDA/AS GRAPHITE COMPOSITES

Aging Temperature, °K	Aging Time, Hours	Test Temperature, °K	Weight Loss, % w/w		Mechanical Properties			
			S.B. Shear Specimen	Flexural Specimen	Flexural Strength, MN/m ² (Ksi)	Flexural Modulus, GN/m ² (Msi)	Short Beam Shear Strength, MN/m ² (Ksi)	
533	0	295	-	-	1764 (256)	120 (17.4)	67.5 (9.8)	
		533	-	-	1310 (190)	120 (17.4)	48.9 (7.1)	
533	200	295	1.2	0.5	1412 (205)	121 (17.6)	73.0 (10.6)	
		533	1.3	0.8	1371 (199)	121 (17.6)	57.2 (8.3)	
533	600	295	1.6	1.2	1137 (165)	119 (17.3)	51.0 (7.4)	
		533	2.2	1.6	1440 (209)	109 (15.8)	51.0 (7.4)	
533	1000	295	-	-	1185 (172)	112 (16.2)	42.7 (6.2)	
		561	-	-	1819 (264)	123 (17.9)	102 (14.8)	
561	200	295	2.2	1.3	902 (131)	114 (16.6)	42.7 (6.2)	
		561	2.2	1.3	1261 (183)	122 (17.7)	75.1 (10.9)	
561	400	295	4.3	2.2	1282 (186)	121 (17.5)	57.9 (8.4)	
		561	6.9	3.0	1330 (193)	120 (17.4)	50.3 (7.3)	
561	600	295	12.3	6.9	923 (134)	101 (14.6)	43.4 (6.3)	
		561	12.3	6.9	1330 (193)	120 (17.4)	46.9 (6.8)	
561	1000	295	12.3	6.9	923 (134)	101 (14.6)	49.6 (7.2)	
		561	12.3	6.9	923 (134)	101 (14.6)	26.1 (3.8)	

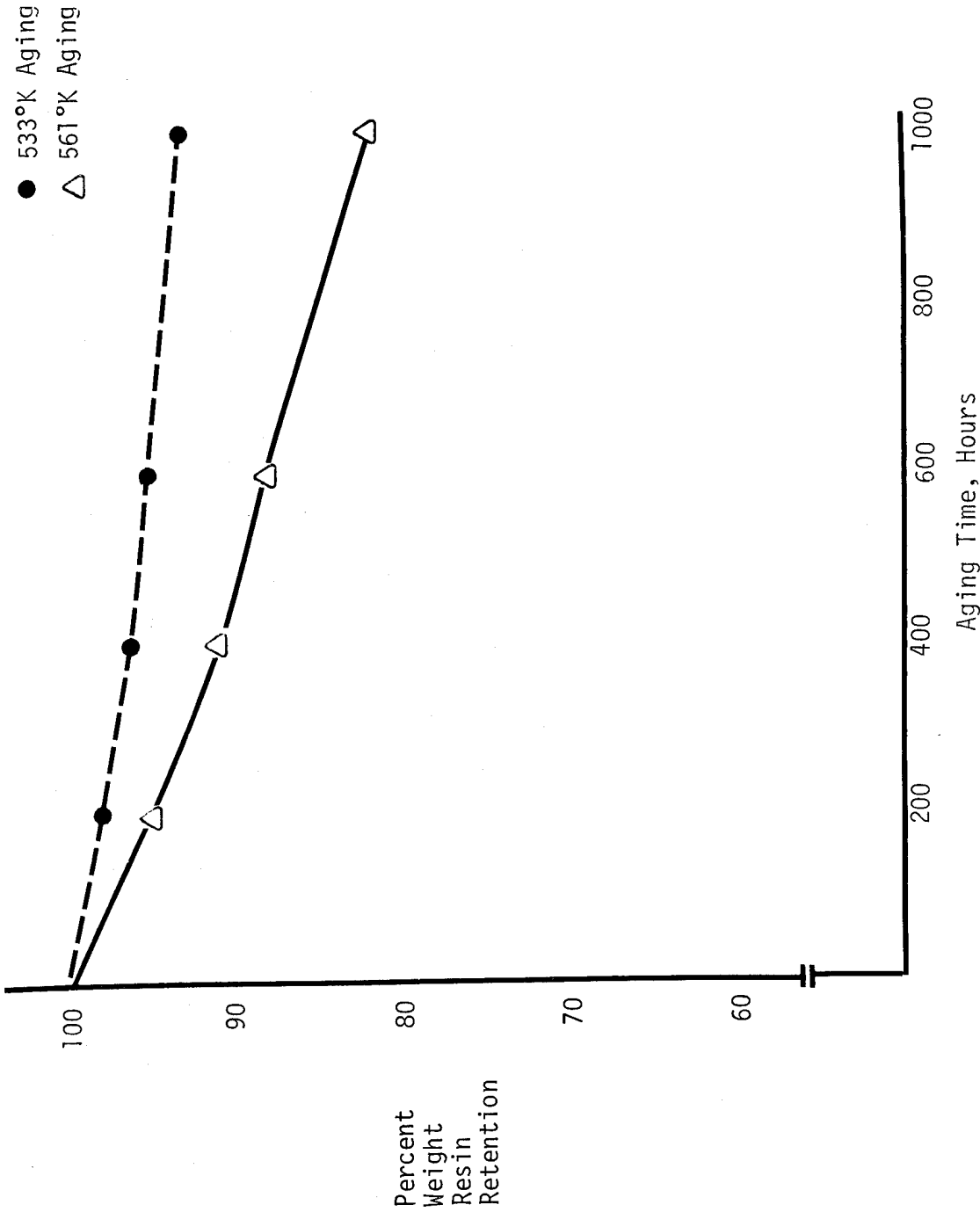


Figure 18. Plot of Resin Weight Retention of PDA Flexural Specimens as a Function of Isothermal Aging at 533°K and 561°K

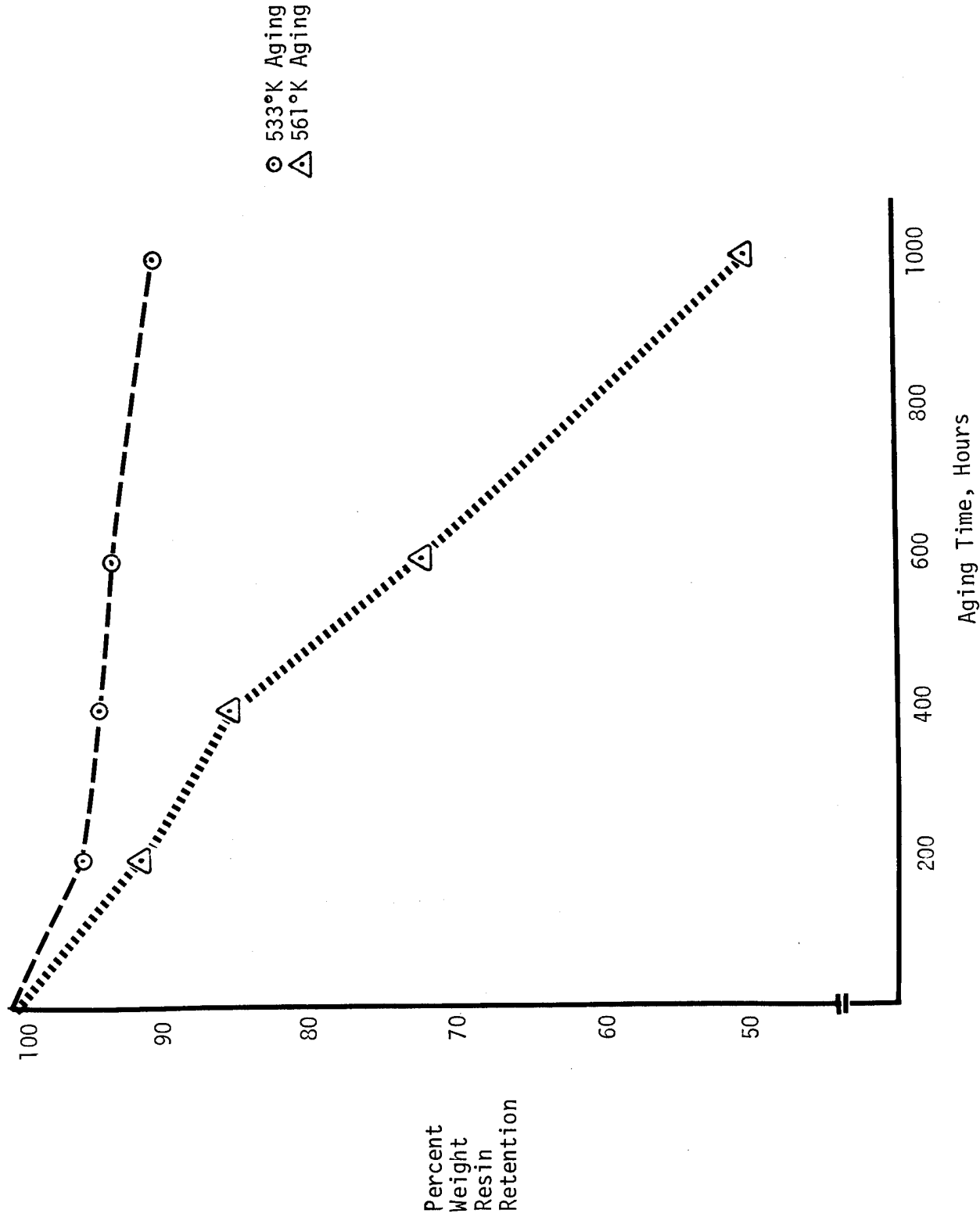


Figure 19. Plot of Resin Weight Retention of PDA Short Beam Shear Specimens as a Function of Isothermal Aging at 533°K and 561°K

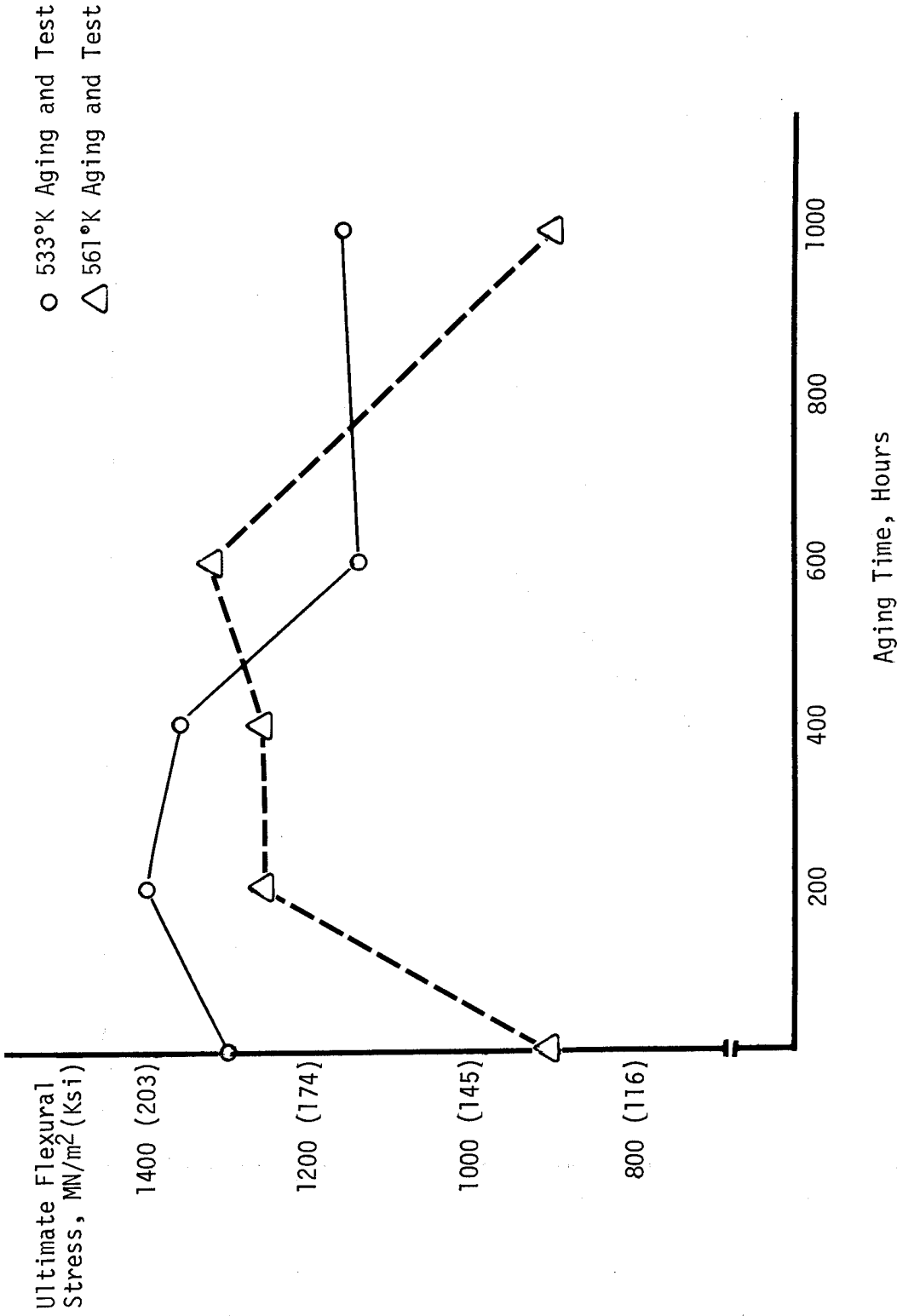


Figure 20. Plot of Ultimate Flexural Stress as a Function of Isothermal Aging at 533°K and 561°K

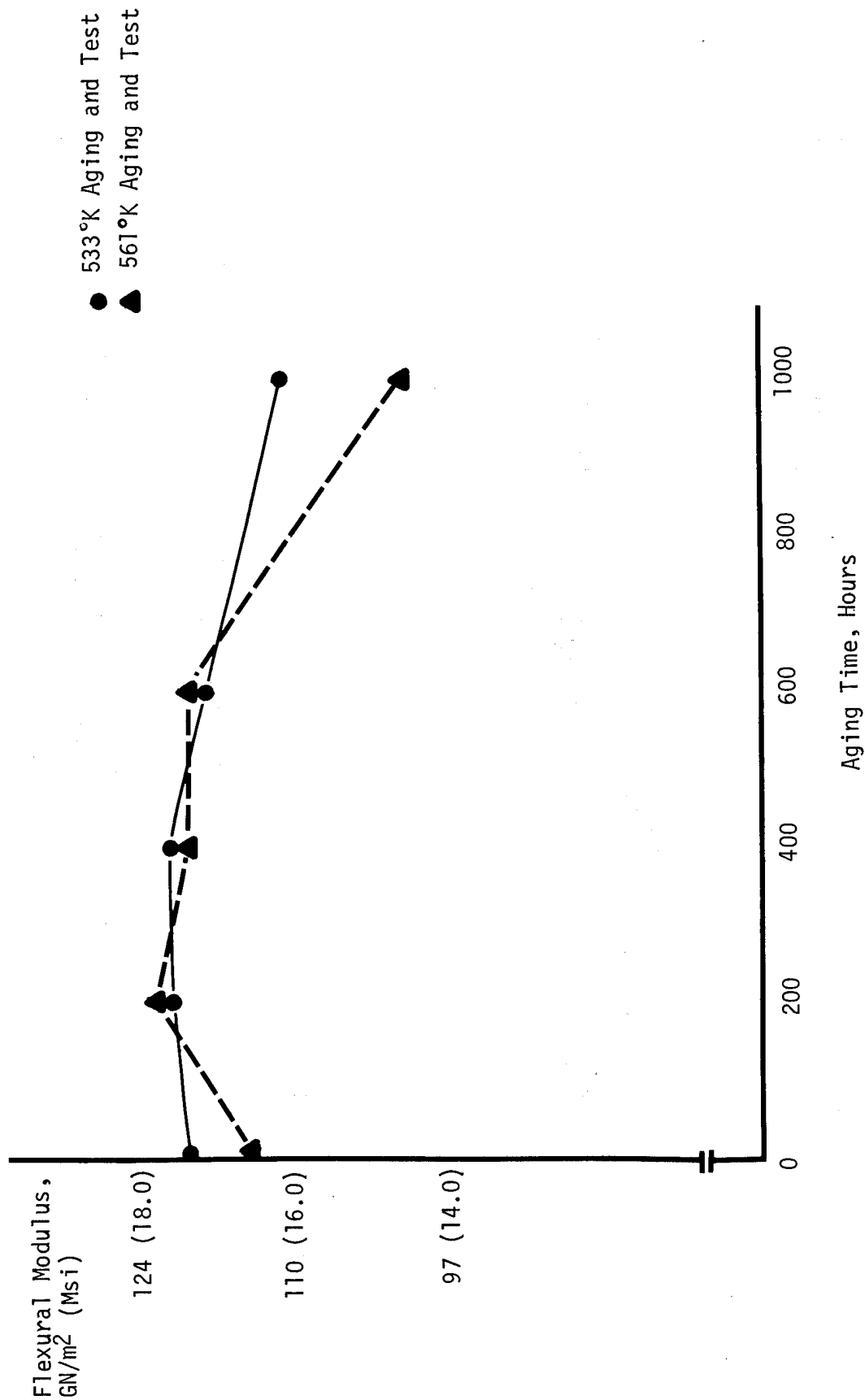


Figure 21. Plot of Flexural Modulus as a Function of Isothermal Aging at 533°K and 561°K

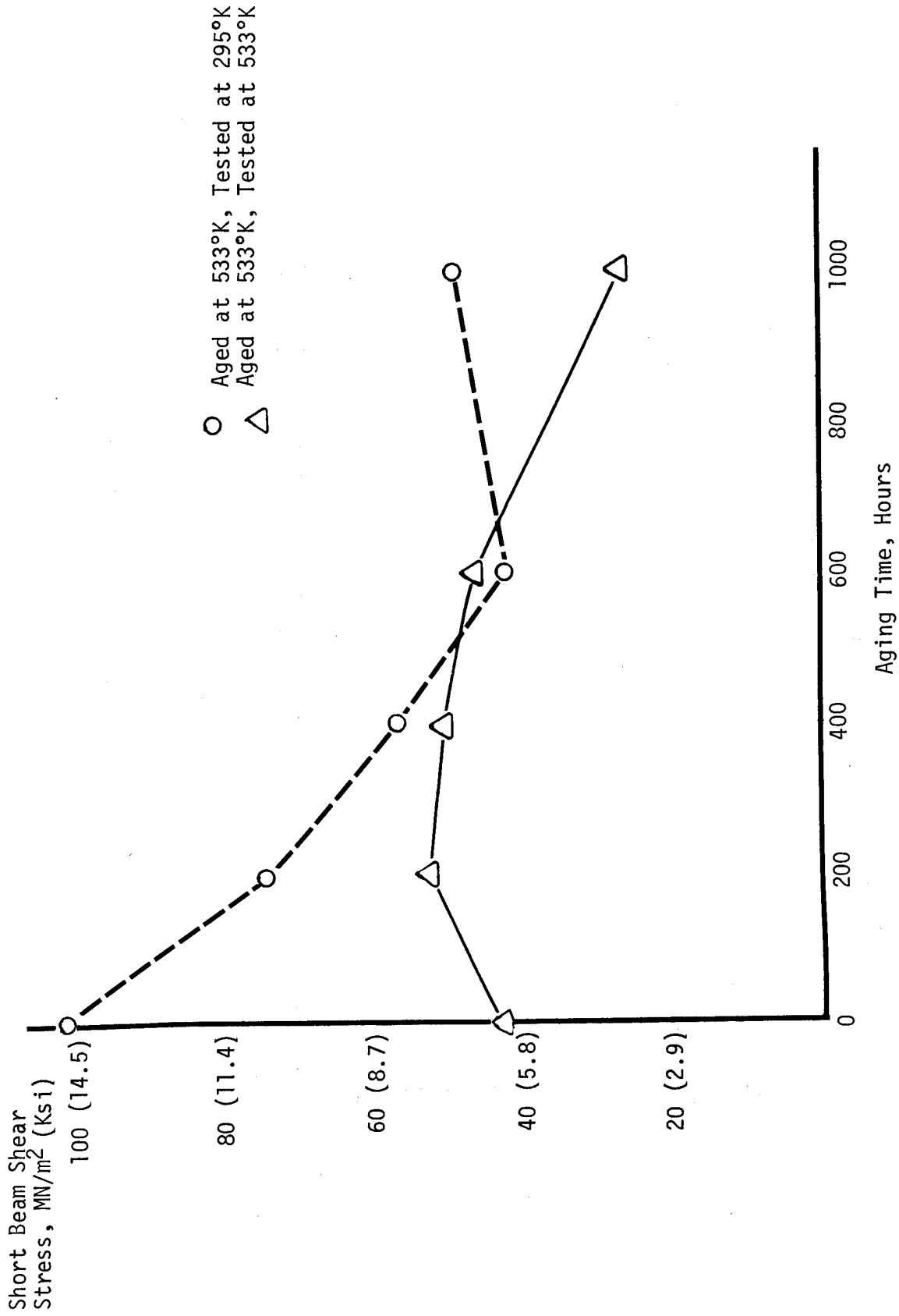


Figure 22. Plot of Short Beam Shear Stress as a Function of Isothermal Aging at 533°K

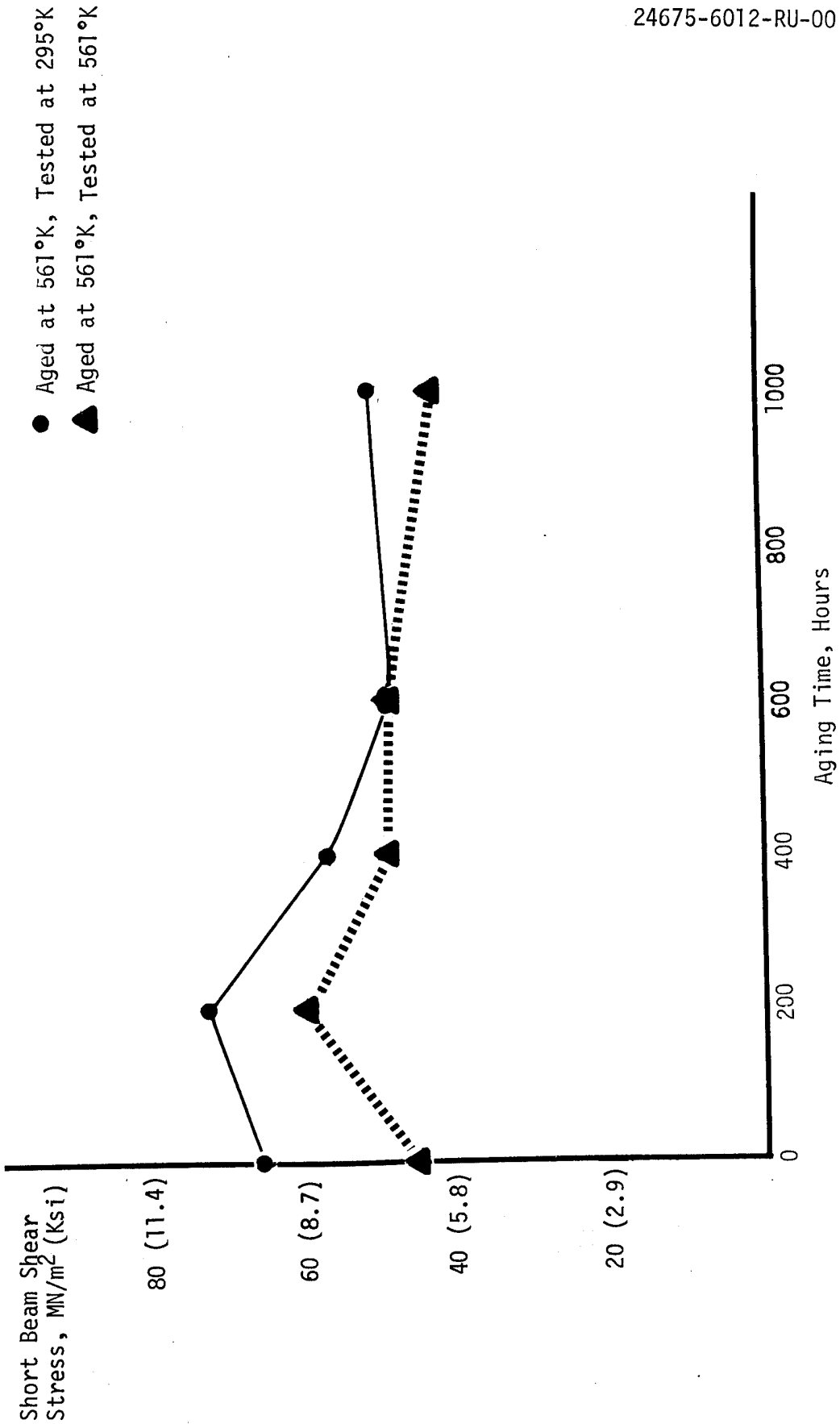


Figure 23. Plot of Short Beam Shear Stress as a Function of Isothermal Aging at 561°K

VI. 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 $\leq 477^\circ\text{K}$. Based on the findings, recommendations are given for further material and process improvement studies.

6.1 CONCLUSIONS

1. Polymer studies have shown that a poly(Diels-Alder) approach employing monomeric ingredients is suitable for autoclave composite fabrication at temperatures below 477°K (400°F).
2. 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 most promising ingredient candidate for autoclave fabrication of high performance A-S reinforced composites at goal process parameters of temperature = 473°K (390°F); pressure = 0.7 MN/m^2 ; duration = 2 hours.
3. A tersolvent combination of acetone: methanol: dioxane was determined to be a vastly improved varnish solvent than either dimethyl formamide (DMF) or N-methylpyrrolidinone (NMP).
4. A staged postcure cycle up to 589°K (600°F) was shown to be most effective for final staging of PDA resins to yield A-S reinforced composites demonstrating high initial mechanical properties.
5. A-S reinforced composites prepared by the resin/solvent/process summarized in 2, 3 and 4 above, are suitable for long-term (>1000 hours) use in air at 533°K (500°F) to 561°K (550°F).

6.2 RECOMMENDATIONS FOR FURTHER STUDY

1. Variations in ingredient formulary should be investigated for the PDA approach to optimize processability/property trade-offs for 1) autoclave cure at 422°K (300°F) to 477°K (400°F), 2) definition of zero defect parts and 3) upgrade the system for long-term use at 589°K (600°F).
2. Postcure studies should be conducted on promising PDA derived resins to render post-treatment to a minimum temperature/time duration.
3. Additional tersolvent studies should be conducted to optimize prepreg quality and shelf-stability.

VII. NEW TECHNOLOGY

This section provides discussions of a new solvent/process developed during this program to prepare A-S-type modulus graphite reinforced composites by autoclave processes which eliminates the requirement for expensive and suspect hazardous solvents such as dimethyl formamide (DMF) and yields higher mechanical properties. The concept believed to be of sufficient novelty that a invention disclosure has been submitted to the TRW Patent Office. This disclosure (designated TRW Document Numer 74-167) is described below.

7.1 TERSOLVENT FOR PROCESSING THE PDA RESIN

A process for preparing graphite reinforced composites employing a PDA monomeric composition of bis(4-maleimidophenyl) methane (BMPM) and bis(furfuryl) benzophenone tetracarboxylic imide (or preferrably the amide acid) was developed in which the resin is prepared in a tersolvent for prepreg manufacture. The preferred process consists of impregnation of the fiber with the resin at 26% w/w solids concentration in a tersolvent consisting of a 4:3:3 mixture by weight of dioxane:methanol:acetone. The tape is then dried overnight at room temperature and the total volatile content of the tape is then adjusted to 18-20% w/w. The prepreg then is cut to the desired length and width dimensions and several plies are stacked to effect a proper thickness. The prepreg then is bagged employing Kapton and introduced into an autoclave. The lay-up is cured employing the following cycle. The initial vacuum bag pressure is set at 50.8 KN/m^2 (15 in.) and the assembly is heated to 377°K (220°F) for 2 hours. The assembly then is heated to 433°K (320°F) and held for 30 minutes. Full vacuum pressure (i.e., $94.8 - 98.2 \text{ KN/m}^2$) and 0.7 MN/m^2 cure pressure then are applied and the assembly is heated to 473°K (390°K) for 2 hours and is then cooled to room temperature under vacuum bag pressure. The composite is postcured by a cycle that includes 1 hour each at 478°K (400°F), 490°K (425°F), 505°K (450°F), 518°K (475°F), 533°K (500°F), 546°K (525°F), then 16 hours at 561°K (550°F), and finally 4 hours at 589°K (600°F).

The finished composite prepared by this total process possesses an excellent combination of properties [e.g., <2% voids, 1905 MN/m^2 (271 Ksi) flexural strength and 78.0 MN/m^2 (11.1 Ksi) short beam shear strength]. The composite products are suitable for long-term use in air at 533°K to 561°K (500°F to 550°F).

APPENDIX A

SYNTHESIS AND CHARACTERIZATION OF MODEL COMPOUNDS

The model compound utilized in Task I studies to investigate the *in situ* aromatization reaction was prepared and characterized as described below.

A.1 MODEL COMPOUND SYNTHESIS

A.1.1 Synthesis of N-Phenyl Maleimide (I)

To a solution of 392.2 g (4.0 mole) of maleic anhydride in 1000 ml of dimethyl formamide was slowly added 372.5 g (4.0 mole) of aniline at such a rate as to maintain the temperature below 323°K while cooling the reaction with an ice-bath. After the addition was complete, 36.8 g (0.4 mole) of anhydrous sodium acetate and 448.8 g (4.4 mole) of acetic anhydride were added. The mixture was then stirred for three hours at 323°K, allowed to cool and then poured into 6000 ml of water. The crude product was air dried and then recrystallized from methanol to give 690 g (80%) of the desired N-phenyl maleimide; mp 363-365°K (90-92°C).

A.1.2 Preparation of N-Furfuryl Phthalimide (II)

To a 1-l. flask equipped with a stirrer, Dean-Stark trap and condenser were added 148.1 g (1 mole) of phthalic anhydride and 600 ml of toluene. The mixture was heated to near reflux during which time most of the anhydride went into solution. To this solution was added dropwise 97.1 g (1 mole) of furfuryl amine and the mixture was then refluxed for 40 hours. At the end of this period the mixture was treated with carbon, filtered and allowed to cool. The resulting light tan precipitate was collected by filtration, washed with a little toluene and air dried. The crude imide was recrystallized from ethanol to give 174 g (77%) imide as a colorless solid; mp 390-391°K (117-118°C). The infrared spectrum contains two carbonyl bands at 1710 and 1765 cm^{-1} (Figure A.1). The nmr spectrum (Figure A.2) is consistent for the assigned structure and the band assignment follows: The aromatic protons signal appears as a multiplet centered at 2.32 τ and the protons on the furan ring exhibit two multiplets centered at 2.72 τ and 3.73 τ . Upfield at 5.25 τ there is a singlet appropriate for the methylene protons.

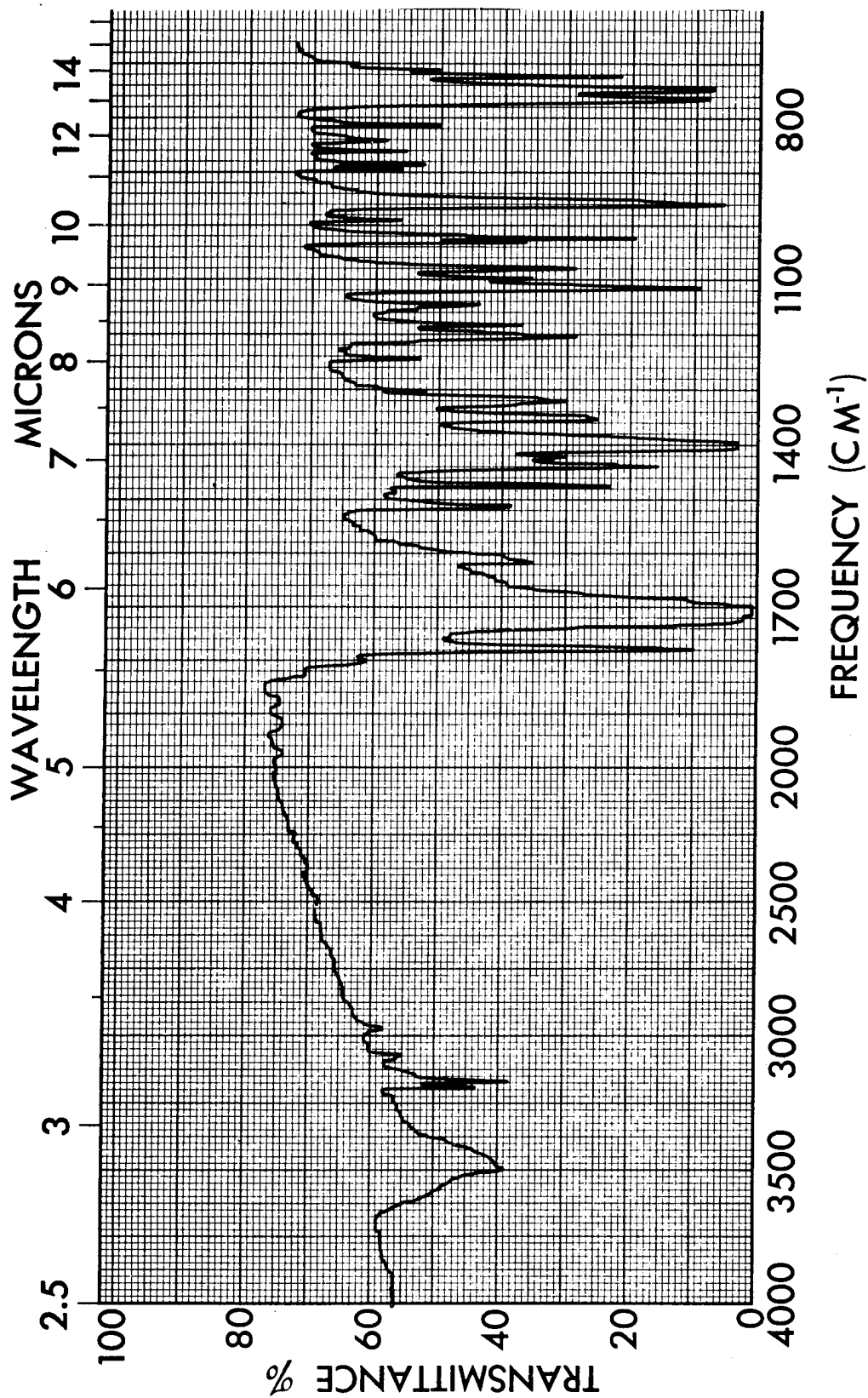


Figure A.1. Infrared Spectrum of N-Furfuryl Phthalimide
Concentration: 3.1 mg/g KBr

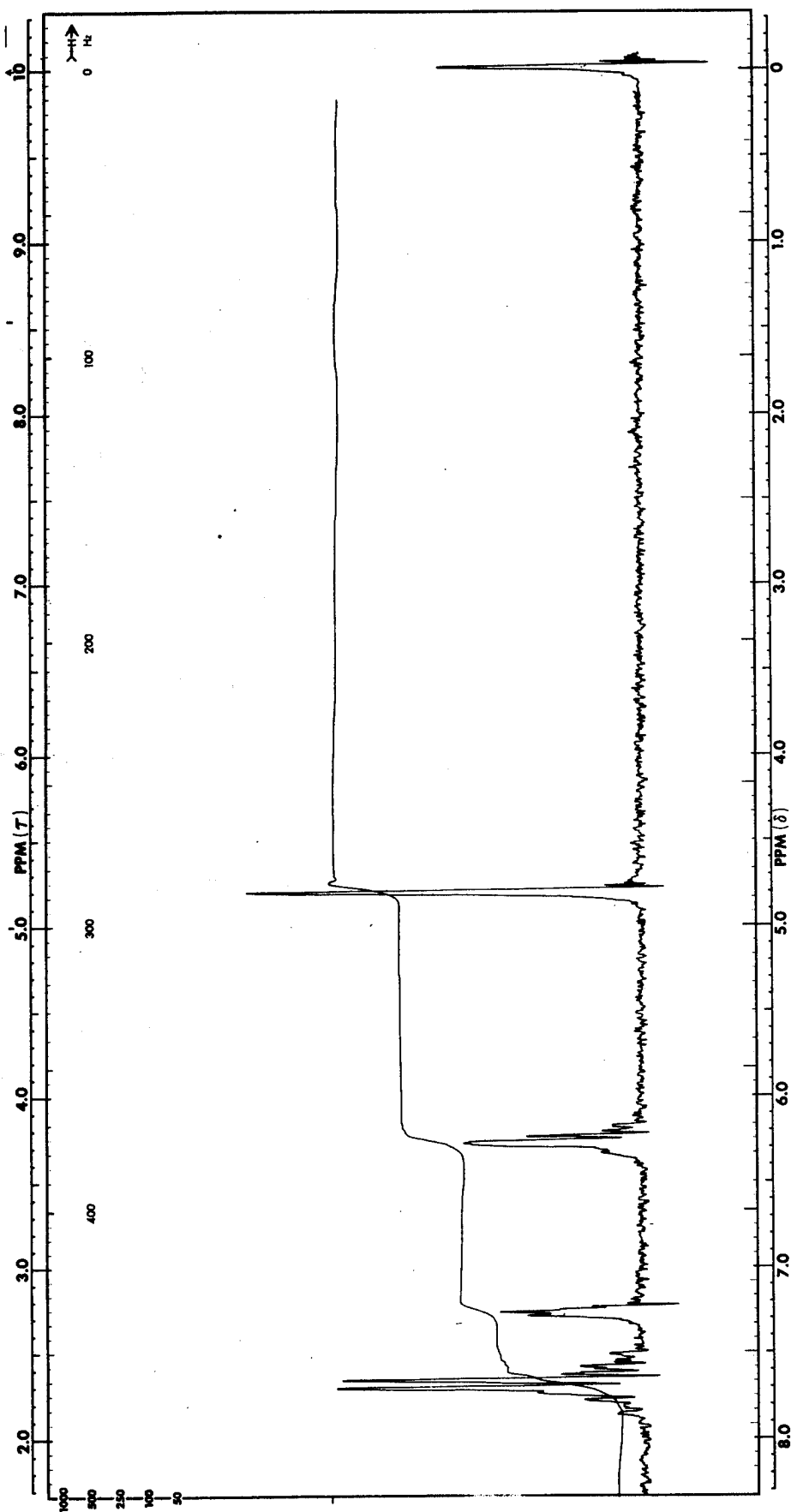


Figure A.2. Nuclear Magnetic Resonance Spectrum of N-Furfuryl Phthalimide
Solvent: CDCl₃

A.1.3 Preparation of Oxygen Bridged Adduct (III)

This reaction was initially run in three different solvents. Ethanol was found to be the best solvent and the procedure used to prepare a large quantity of material is described below.

A mixture of 45.4 g (0.2 mole) of N-furfuryl phthalimide and 34.6 g (0.2 mole) of N-phenyl maleimide in 1200 ml of ethanol was refluxed for 18 hours. At the end of the reflux period a significant amount of precipitate was present. The mixture was cooled and the precipitate was then collected by filtration and dried to yield 61.5 g (77%) of adduct; mp 440-443°K (167-170°C). An analytical sample was recrystallized from acetonitrile; mp 442-444°K (169-171°C). The infrared spectrum for this compound is shown in Figure A.3. A physical blend of Compound I and Compound II was prepared and an ir spectrum obtained. (Figure A.4.)

The nmr spectrum of the adduct, Figure A.5, is also consistent with the assigned structure. The two sets of aromatic protons appear as multiplets centered at 2.27 τ and 2.63 τ . The small sharp peak at 2.78 τ is attributed to the chloroform in the solvent and the peak upfield at 3.22 τ appears to be appropriate for the vinyl protons on N-phenyl maleimide indicating a small amount unreacted starting material present in the adduct. The vinyl protons are again a multiplet at 3.50 τ and the allylic proton signal appears at 4.73 τ . The protons at C-2 and C-3 on the oxynadic ring appear as a multiplet 5.53 τ and the singlet for the methylene protons is upfield at 6.90 τ .

A.1.4 Characterization of *in situ* Aromatization Samples

Shown in Figures A.6 through A.9 are the nmr spectra of the samples obtained from the *in situ* aromatization study on Compound III. The results obtained from this study were discussed in Section 2.1.2.

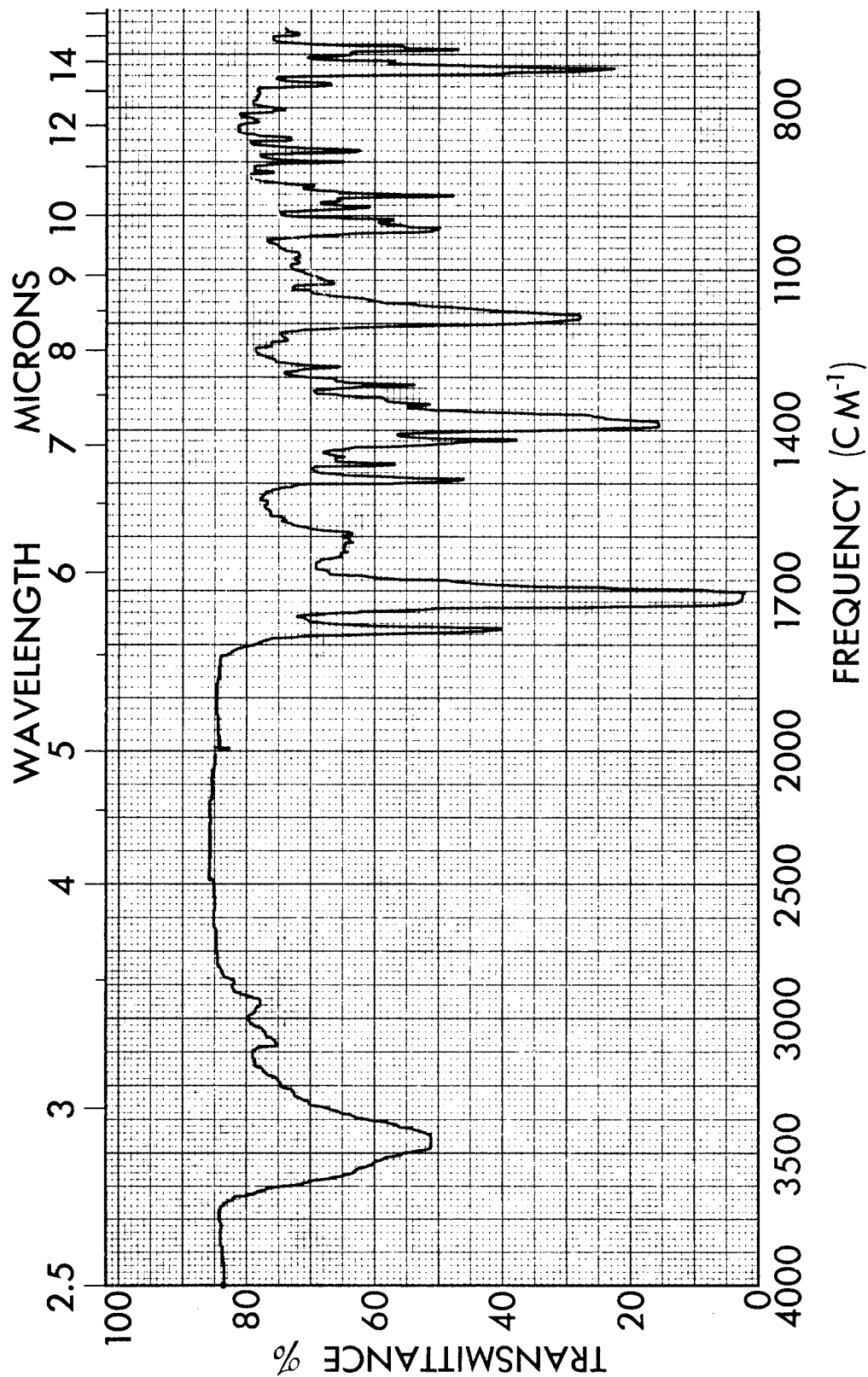


Figure A.3. Infrared Spectrum of Oxygen Bridged Adduct, III
Concentration: 3.0 mg/g KBr

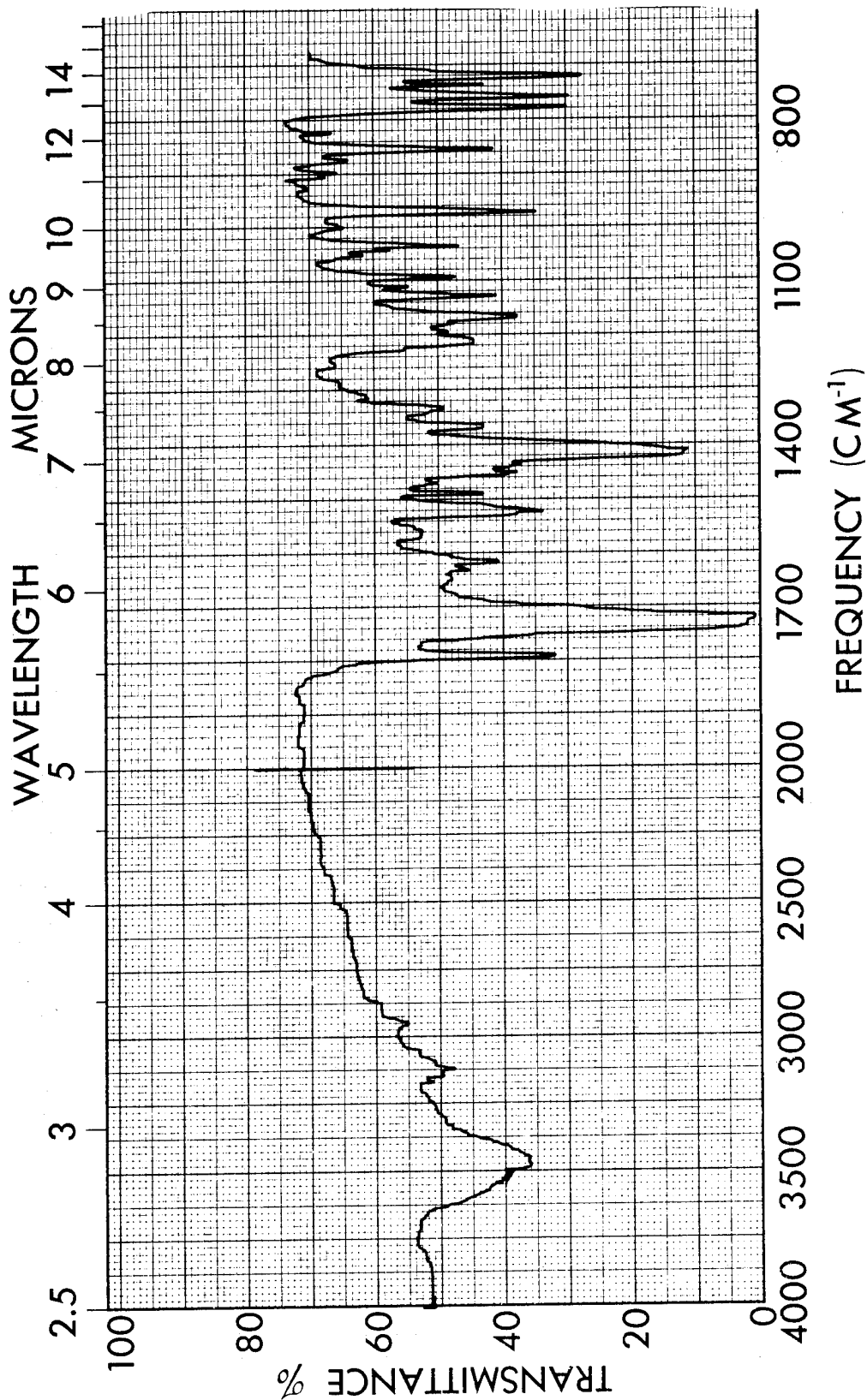


Figure A.4. Infrared Spectrum of a Physical Blend of a Equal Molar Mixture of Compounds I and II
Concentration: 3.0 mg/g KBr

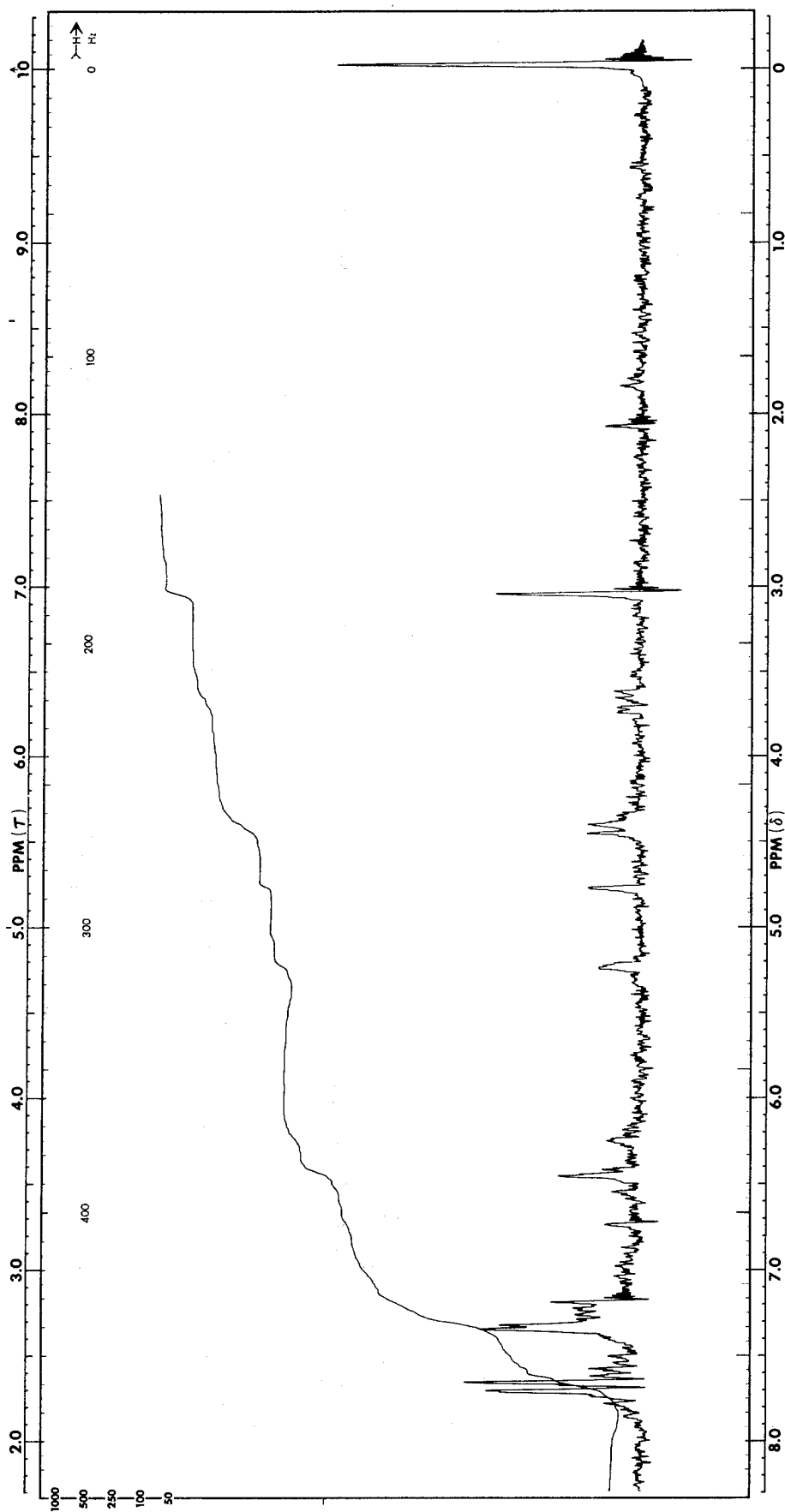


Figure A.6. Nuclear Magnetic Resonance Spectrum of Oxygen Bridged Adduct,
III Heated at 450°K (350°F) for Two Hours
Solvent: CDCl_3

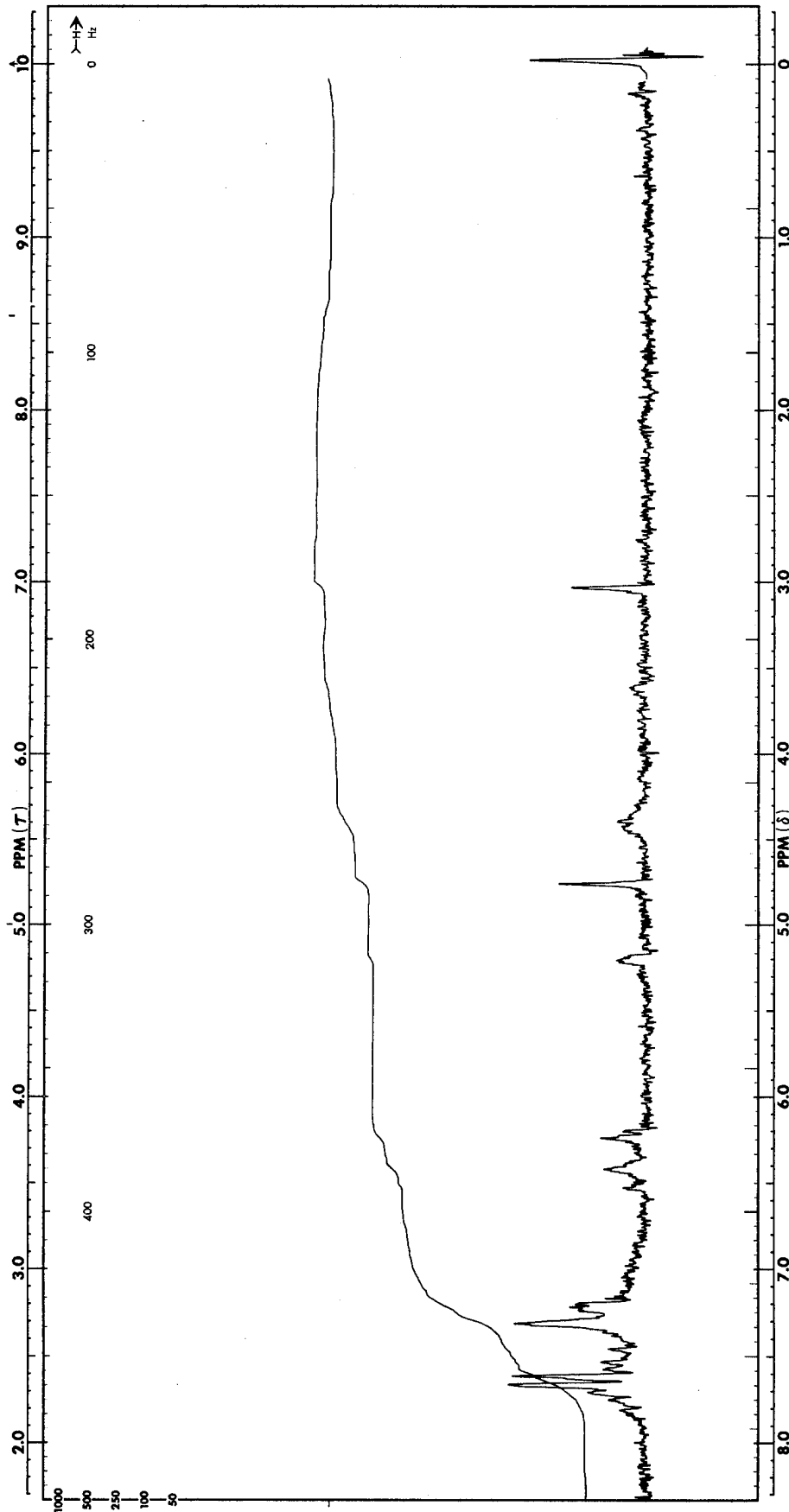


Figure A.7. Nuclear Magnetic Resonance Spectrum of Oxygen Bridged Adduct,
III Heated at 464°K (375°F) for Four Hours
Solvent: CDCl_3

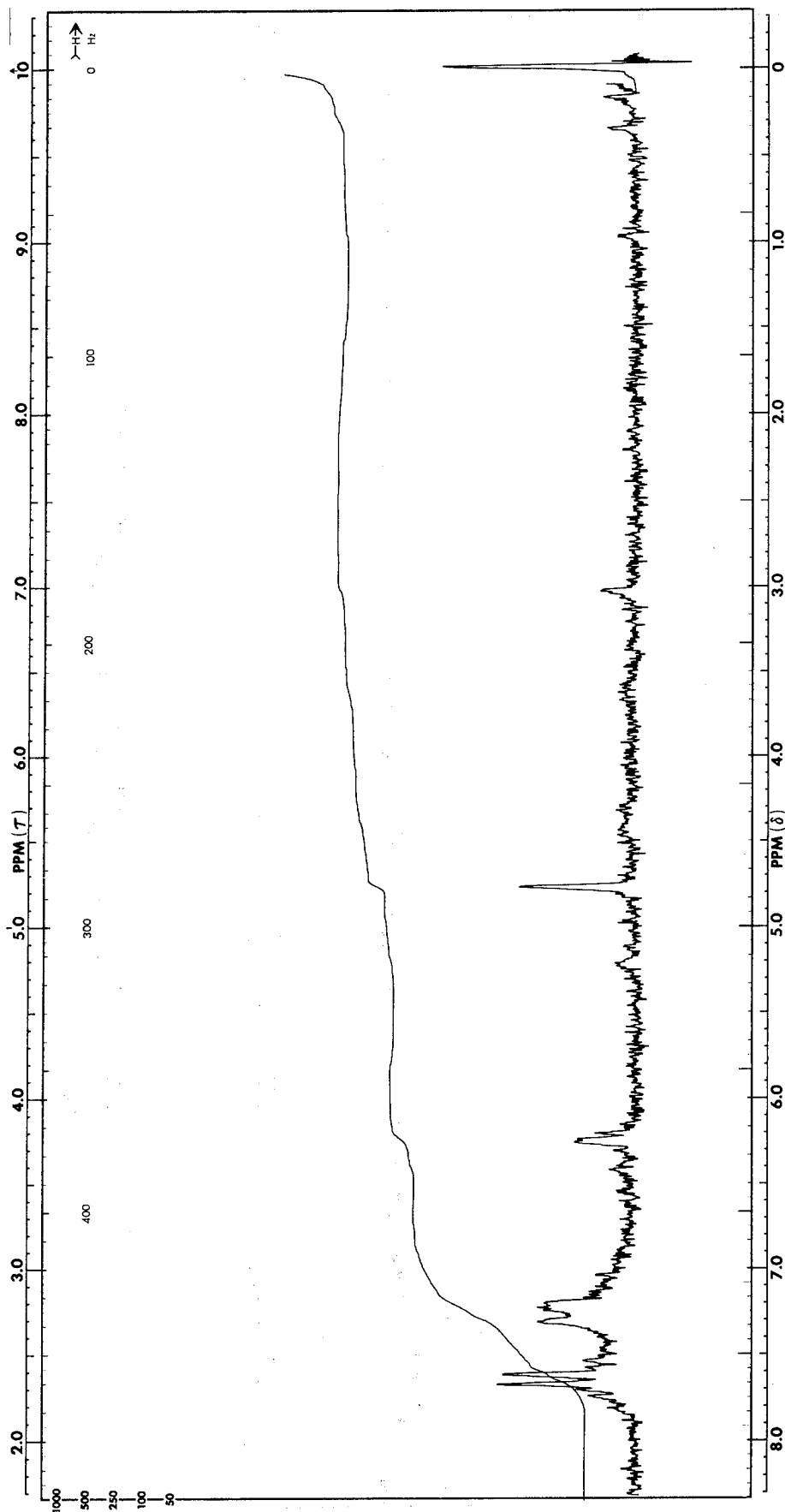


Figure A.8. Nuclear Magnetic Resonance Spectrum of Oxygen Bridged Adduct,
III Heated at 464°K (375°F) for Six Hours
Solvent: CDCl_3

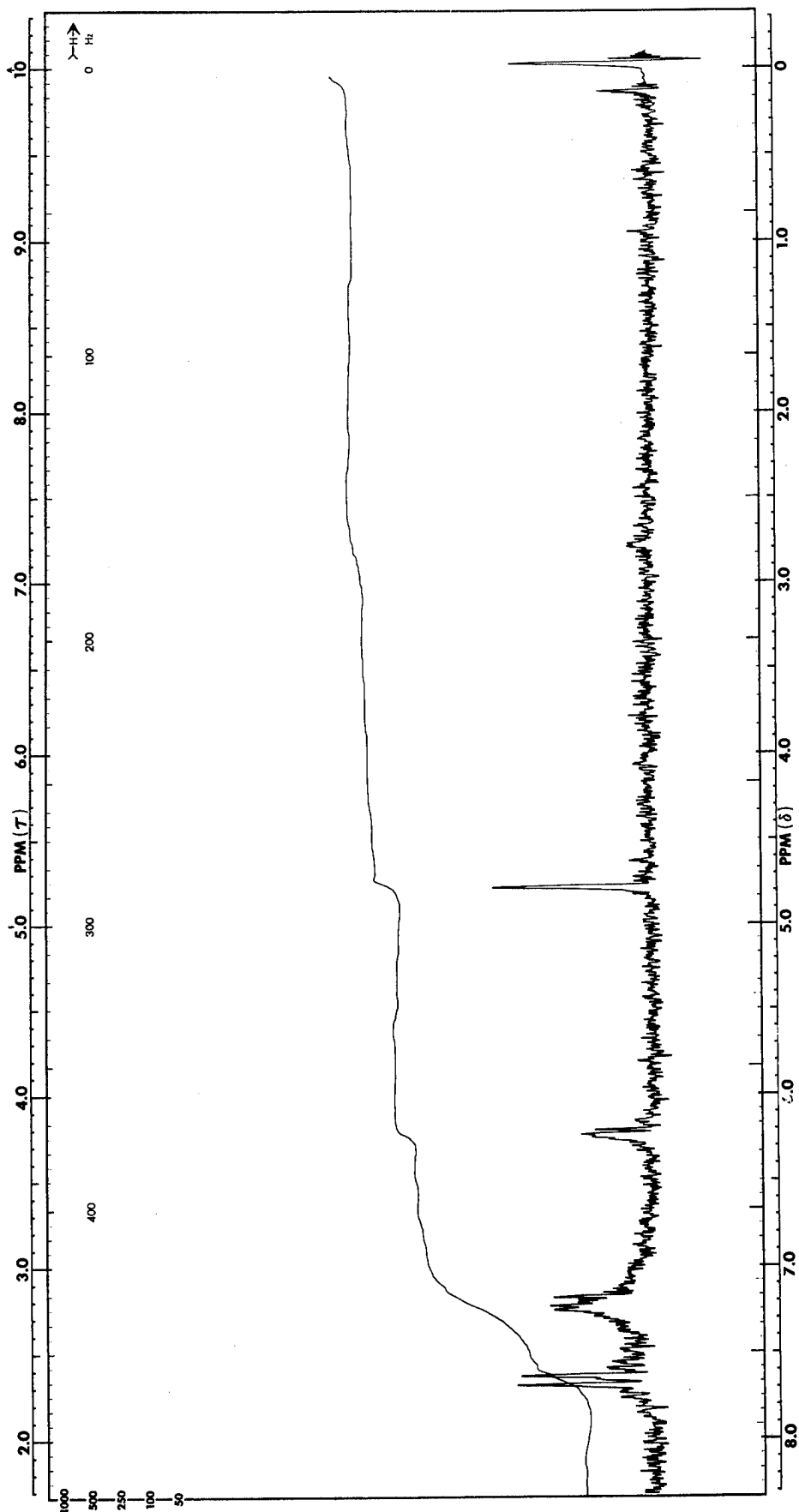


Figure A.9. Nuclear Magnetic Resonance Spectrum of Oxygen Bridged Adduct,
III Heated at 505°K (450°F) for Two Hours
Solvent: CDCl_3

APPENDIX B

SYNTHESIS AND CHARACTERIZATION OF MONOMERS

The synthesis procedures used to prepare the monomers used to prepare the resins studied in this program are described below.

B.1 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 were 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.1 and Figure B.2, respectively.

B.2 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.3 and Figure B.4, respectively.

B.3 PREPARATION OF BIS(4-MALEIMIDOPHENYL) ETHYLENE (BMPE)

To a stirred solution of 14.72 g (0.07 mole) of 4,4'-diaminostilbene in 20 ml of DMF under a nitrogen atmosphere was added a solution of 13.72 g (0.14 mole) of maleic anhydride in 50 ml of DMF over a 20 minute period.

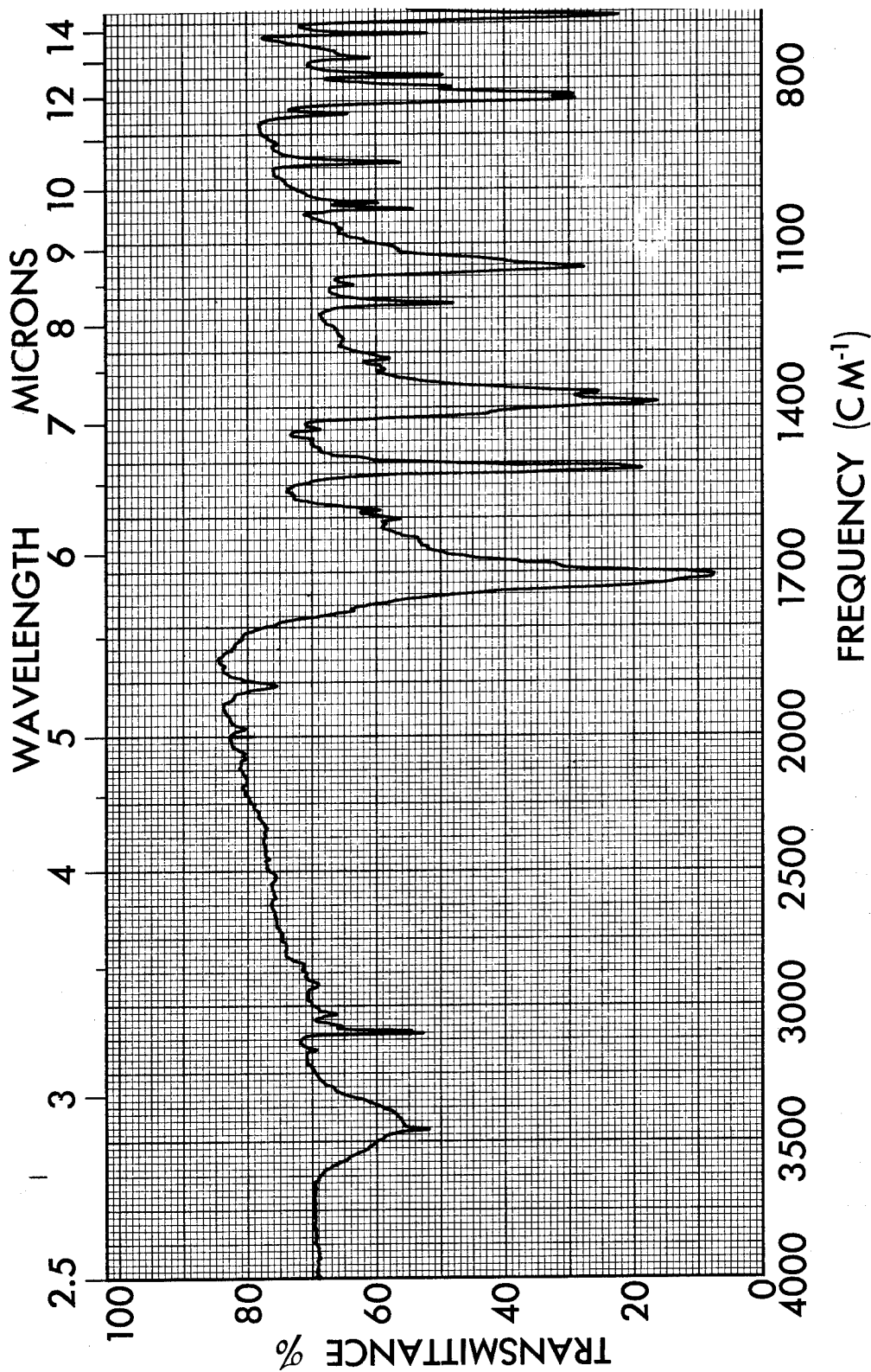


Figure B.1. Infrared Spectrum of Bis(4-maleimidophenyl) methane (KBr)
Concentration: 3.1 mg/g (KBr)

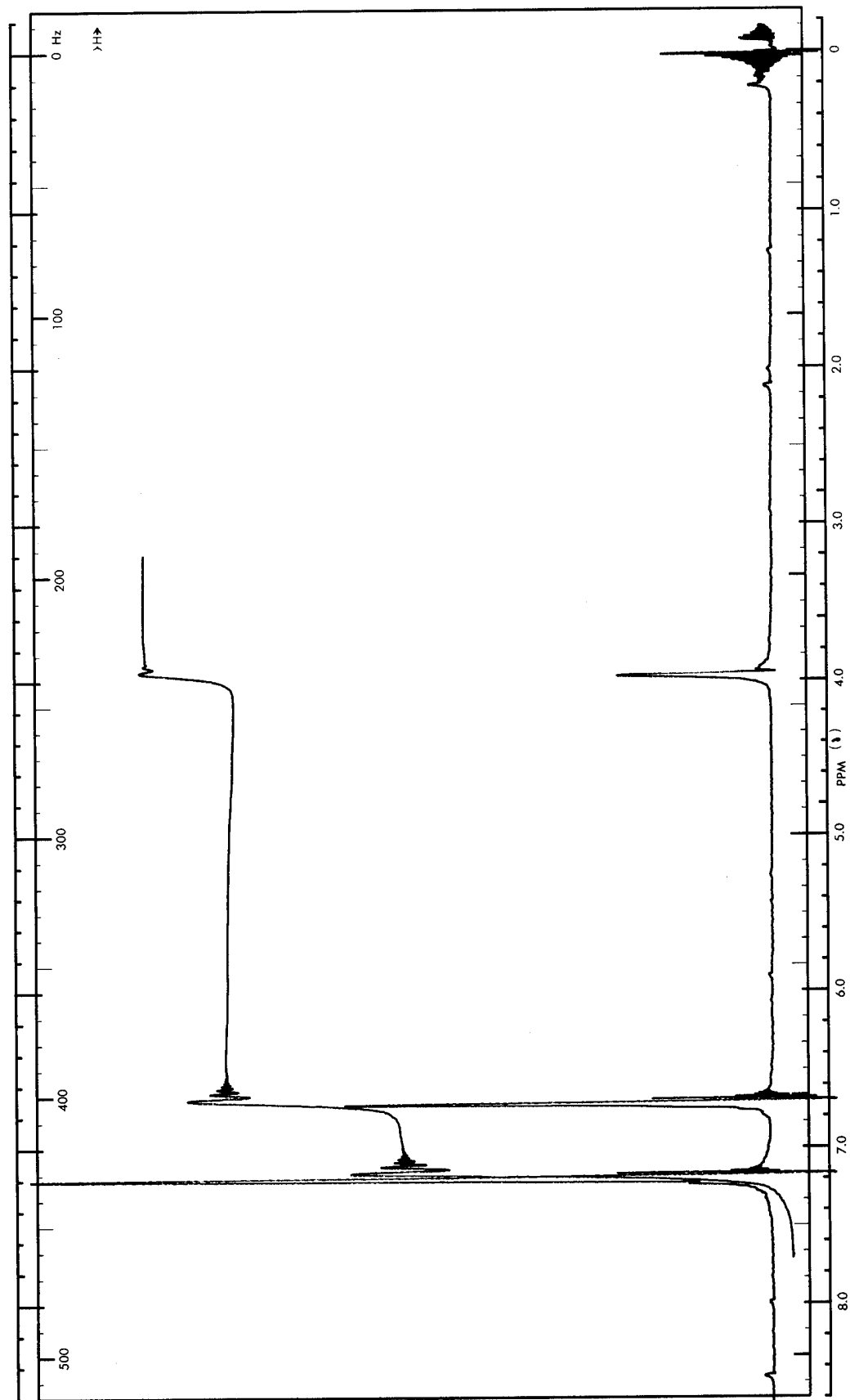


Figure B.2. Nuclear Magnetic Resonance Spectrum of
Bis(4-maleimidophenyl) Methane
Solvent: DMSO₆

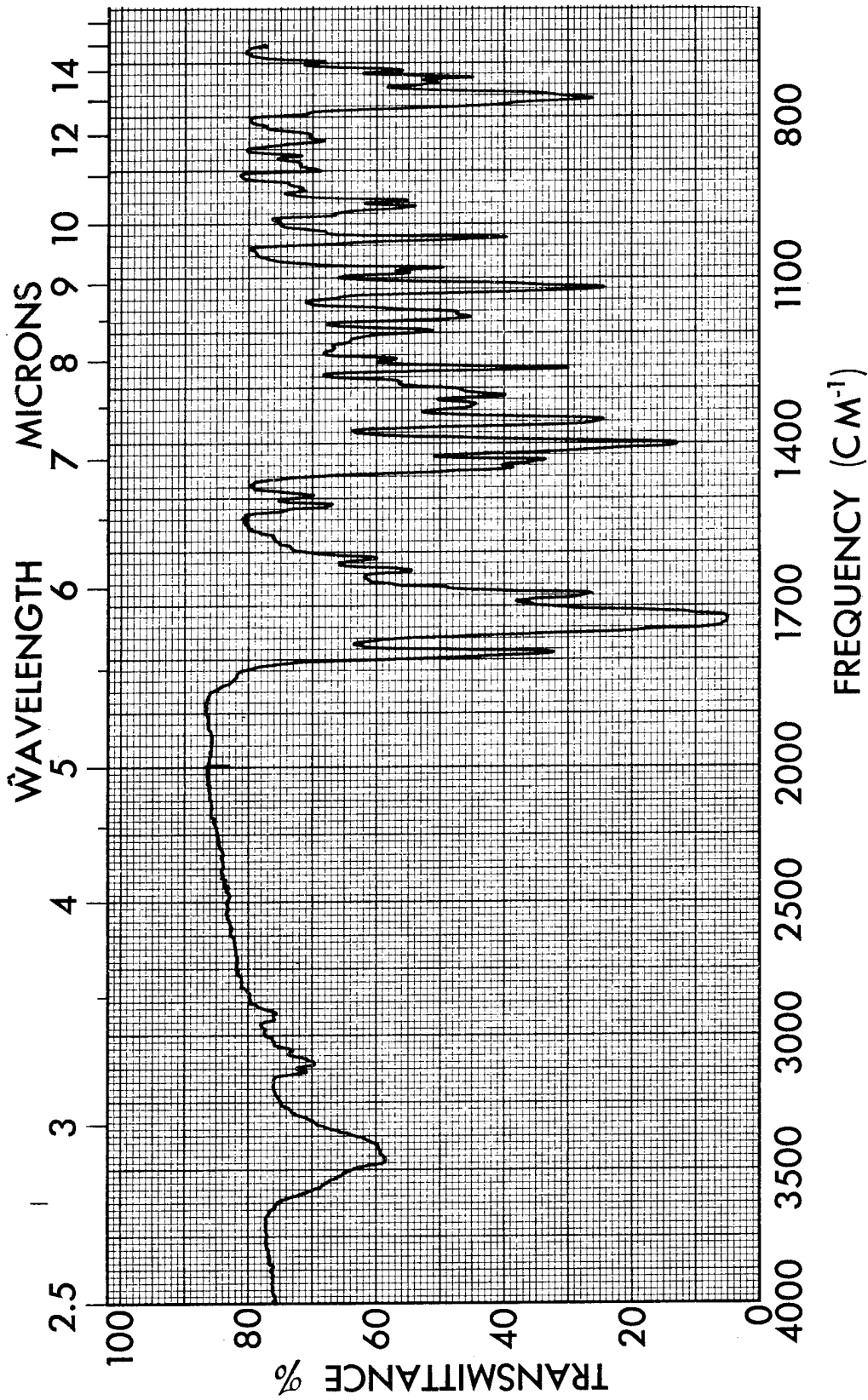


Figure B.3. Infrared Spectrum of Bis(2-furfuryl) Benzophenone Tetracarboxylic Imide
Concentration: 3.0 mg/g KBr

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The mixture was stirred for an additional 30 minutes after the addition was complete and then 17.85 g (0.175 mole) of acetic anhydride and 1.43 g (0.0175 mole) of sodium acetate were added to the mixture. The reaction mixture was heated at 323°K for three hours and then allowed to cool. The bismaleimide was precipitated by adding the DMF solution to 600 ml of water. The crude product was collected by filtration, dried and then recrystallized from a 1:1 (v/v) mixture of DMF and ethanol. The light yellow colored bismaleimide failed to melt below 573°K and because of its low solubility in common organic solvents nmr analysis was not performed. The infrared spectrum for the compound is shown in Figure B.5 and is consistent for the maleimide structure.

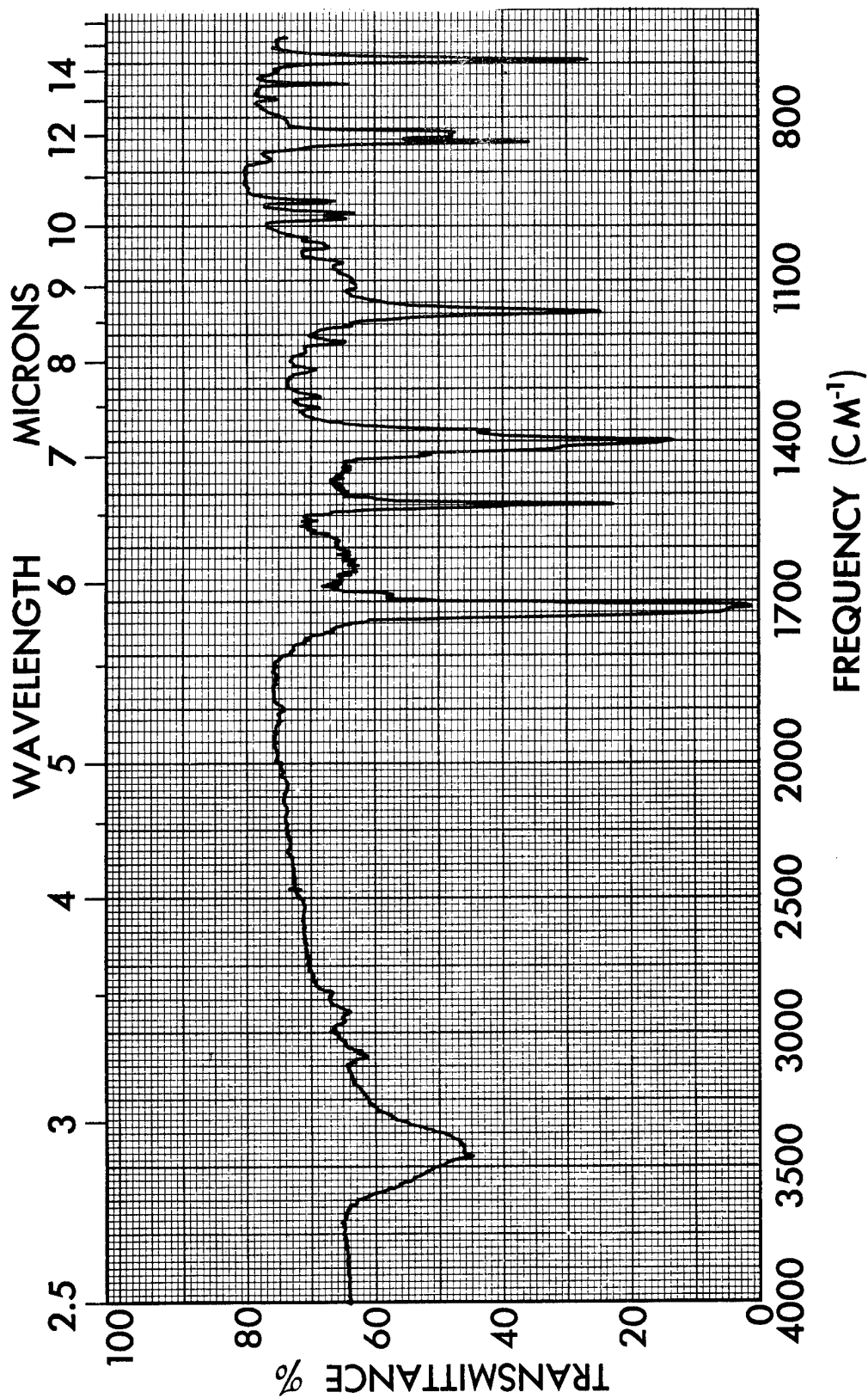


Figure B.5. Infrared Spectrum of Bis(4-maleimidophenyl) ethylene
Concentration: 3.1 mg/g KBr

APPENDIX C

PREPARATION OF PDA VARNISH

The procedure employed to prepare the PDA varnish in the tersolvent is given below.

C.1 PREPARATION OF PDA VARNISH IN THE TERSOLVENT

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

APPENDIX D.
TEST PROCEDURES FOR CHARACTERIZATION
OF GRAPHITE TAPE AND COMPOSITES

D.1 GRAPHITE TAPE CHARACTERIZATION

D.1.1 Volatile Matter

Volatile content of graphite prepreg was determined by thermally treating a tarred sample for 30 minutes at 561⁰K (550⁰F). After cooling to R. T., the specimen was reweighed and the volatile content was calculated by the following formula:

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

Where:

W_1 = Weight Sample

W_2 = Weight Sample After Heat Aging

D.1.2 Resin Content

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

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

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

Where:

W_{wr} = Wet Resin Content

W_{dr} = Dry Resin Content

W_1 = Weight Sample

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

D.2 COMPOSITE CHARACTERIZATION

D.2.1 Graphite Composite Resin Content

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

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

Where:

W_r = Weight Content of Resin Solids, % w/w

W_1 = Weight of Cured Composite Sample

W_2 = Weight of Filaments after Acid Digestion of the
Resin Matrix

D.2.2 Density of Composites

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

formula:

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

Where:

W_A = Weight Sample in Air

W_W = Weight Sample in Water

D.2.3 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, %

D_C = Measured Density of Composite, g/cm³

D_f = Density of Fiber, g/cm³

K = Weight Fraction, Resin

The specific gravity of the Hercules A-S fiber is 1.76 g/cm³.

D.2.4 Composite Void Content

Void contents of the composites were calculated using the formula:

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

Where:

V_V = Volume of Voids, % v/v

D_C = Measured Density of Composite, g/cm³

D_r = Density of Resin, g/cm³

D_f = Density of Fiber, g/cm³

W_r = Weight Content of Resin, %

W_f = Weight Content of Fiber, %

D.2.5 Shear Strength of Composites

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

Shear strengths were calculated using the simple formula:

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

Where:

- S_u = Ultimate Shear Strength, MN/m²
- V = Load at Failure, N
- t = Specimen Thickness, mm
- b = Specimen Width, mm

D.2.6 Flexural Properties of Composites

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

Flexural strengths and moduli were calculated using the formulae:

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

and

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

Where:

- F_u = Stress in the Outer Fiber at Mid-span, MN/m²
- E_b = Modulus of Elasticity in Bending, GN/m²
- P = Load at Failure, N
- L = Span, mm

b = Width of Specimen, mm

d = Thickness of Specimen, mm

m = Slope of the Tangent to the Initial Straightline
Portion of the Load Deflection Curve, N/mm

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