NASA CR-135377
TRW ER-7884 F

TRW
EQUIPMENT GROUP

FIBER REINFORCED PMR POLYIMIDE COMPOSITES

BY

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NASA LEWIS RESEARCH CENTER

CONTRACT NAS 3-20366

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RAYMOND D. VANNUCCI

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                         ***DTIC DOES NOT HAVE THIS ITEM***
-- 1 - AD NUMBER: D425473
-- 3 - ENTRY CLASSIFICATION:   UNCLASSIFIED
-- 5 - CORPORATE AUTHOR: TRW EQUIPMENT GROUP  CLEVELAND OHIO
-- 6 - UNCLASSIFIED TITLE:     FIBER REINFORCED PMR POLYIMIDE COMPOSITES.
-- 8 - TITLE CLASSIFICATION:   UNCLASSIFIED
-- 9 - DESCRIPTIVE NOTE: FINAL REPT., 28 JUN 76 - 31 OCT 77,
--10 - PERSONAL AUTHORS: CAVANO ,P. J. ;WINTERS,W. E. ;
--11 - REPORT DATE:       MAY 15, 1978
--12 - PAGINATION:    105P
--14 - REPORT NUMBER:     ER-7884F
--15 - CONTRACT NUMBER:   NAS3-20366
--18 - MONITOR ACRONYM:   NASA
--19 - MONITOR SERIES:    CR-135377
--20 - REPORT CLASSIFICATION:  UNCLASSIFIED
--22 - LIMITATIONS (ALPHA):    APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
--     UNLIMITED. AVAILABILITY: NATIONAL TECHNICAL INFORMATION SERVICE,
--     SPRINGFIELD, VA. 22161. NASA-CR-135377.
-
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1. Report No.
NASA CR-135377

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle

Fiber Reinforced PMR Polyimide Composites

5. Report Date
May 15, 1978

6. Performing Organization Code

7. Author(s)

P. J. Cavano and W. E. Winters

8. Performing Organization Report No.
ER-7884F

9. Performing Organization Name and Address

TRW Inc.
TRW Equipment
23555 Euclid Avenue
Cleveland, Ohio 44117

10. Work Unit No.

11. Contract or Grant No.
NAS3-20366

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

Commercially obtained PMR-15 polyimide prepregs with S-glass and graphite fiber reinforcements were evaluated along with in-house prepared glass and graphite cloth PMR II materials. A novel autoclave approach was conceived and used to demonstrate that both the PMR systems respond to 1.4 MPa (200 psi) autoclave pressures to produce void-free composites equivalent to die molded laminates. Isothermal gravimetric analysis and subsequent mechanical property tests indicated that the PMR II system was significantly superior in thermo-oxidative stability, and that S-glass reinforcements may contribute to the accelerated degradation of composites at 316°C (600°F) when compared to graphite fiber reinforced composites previously studied under the same conditions. Fully reversed bending fatigue experiments were conducted with a type of fixture previously unused for organic matrix composites. These studies indicated that the graphite fiber composites were clearly superior in fatigue resistance to the glass fiber reinforced material and that PMR matrix composite systems yield performance of the same order as composite materials employing other families of matrices.

17. Key Words (Suggested by Author(s))

Graphite Fiber Composites
PMR-15 Polyimide Resin
PMR II Polyimide Resin
Autoclaved Polyimide Composites
Flexural Fatigue Testing

18. Distribution Statement
Unclassified-Unlimited

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
105

22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

Blank Pages

FOREWORD

This document represents the final report of the work accomplished between June 28, 1976 and October 31, 1977 by TRW Inc. for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, under Contract NAS3-20366 on a program entitled, "Fiber Reinforced PMR Polyimide Composites." This program was conducted under the technical direction of Mr. Raymond D. Vannucci, NASA Project Manager.

Work on the program was conducted at TRW Materials Technology of TRW Equipment, Cleveland, Ohio. Mr. William E. Winters was the TRW Program Manager; the TRW Project Engineer was Mr. Paul J. Cavano.

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FIBER REINFORCED PMR POLYIMIDE COMPOSITES

by

P. J. Cavano and W. E. Winters

SUMMARY

The major objectives of the program were to characterize commercially obtained PMR-15 polyimide prepreg on several reinforcements; develop process cycles for these materials as well as PMR II polyimide prepreg prepared in-house; and investigate long term composite performance on several of the above materials. The excellent performance exhibited by the PMR-15 matrix system, previously well established in the laboratory, has triggered the production of commercial materials now beginning to be used in significant quantities. For this reason, an evaluation of vendor supplied cloth and tape prepreg, as opposed to materials prepared under laboratory conditions, was timely. The PMR II matrix, a second generation PMR, utilizes the same reaction chemistry as the PMR-15 system. PMR II resins have been identified as conferring superior thermo-oxidative stability while retaining the processability of PMR-15. At this time, PMR II is not a commercially available prepreg material. PMR II monomer solutions are available on an experimental basis. Problems associated with the storage and handling of these solutions were investigated.

The program was conducted in three phases: the selection and acceptance of vendor prepared glass and graphite cloth and graphite fiber tape prepreg; the development of die and autoclave fabrication cycles; and the collection of room and elevated static properties, such as flexure and shear, and long term properties, *viz*. isothermal gravimetric analysis at 260°C (500°F) and 316°C (600°F) and fully reversed flexural fatigue.

It was learned that commercial prepregging processes provided PMR-15 cloth materials of high quality with the expected molding and property performance and storage lives out to one year. The unidirectional tape material, at least at the time of purchase from the vendor employed, requires further investigation before a fully satisfactory, reproducible system is available. A new autoclave

process, employing localized part heating as opposed to heating the entire autoclave interior volume, introduced a technique that permits the use of equipment rated for 177°C (350°F) for cures as high as 316°C (600°F). This autoclave process, at 1.4 MPa (200 psi), yielded essentially void-free PMR-glass and -graphite composites with properties equivalent to die molded laminates.

Long term isothermal studies out to 2000 hours confirmed the improved performance of the PMR II system at 316°C (600°F) in air. Composite studies with glass fiber reinforced PMR-15 and PMR II revealed an anomalous, accelerated degradation of composite mechanical properties compared to the performance of graphite fiber reinforced PMR composites.

Fully reversed bending fatigue studies at room temperature indicated that graphite fiber composites were clearly superior in fatigue resistance to the glass fiber reinforced material and that PMR matrix composite systems yield performance of the same order as composite materials employing other families of matrices.

Further work is suggested in confirming and defining the accelerated thermo-oxidative degradation of the S-glass reinforced composites, fatigue studies and investigation of the PMR II system on other reinforcements.

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1.0 INTRODUCTION

This document constitutes the final report on NASA-Lewis Contract NAS3-20366, initiated June 28, 1976, and describes the work performed between that date and October 31, 1977. The major objectives of the program were to characterize vendor supplied PMR-15 prepreg on several reinforcements; develop process cycles for these materials, as well as for PMR II prepreg prepared in-house; and develop long term composite data on several of the materials.

The PMR (Polymerization of Monomeric Reactants) polyimide resins, originally developed by NASA-Lewis personnel, employ three stable monomers (a diamine and two ester-acids) which are mixed in alcohol, applied directly to the reinforcing fibers and reacted in situ. This technique reproducibly yields void-free composites and eliminates such classic problems as prepolymer instability, residual solvents of a high boiling nature and sensitive, complex processing procedures(1)(2). While a large number of government and industry organizations have evaluated the first generation PMR (PMR-15) in tests and prototype applications, significant quantities of this material are now beginning to be used. It was, therefore, timely that a program involving the use of commercially prepared prepreg and investigating material acceptance approaches, processing cycles, and long term properties be conducted. The investigation of the second generation PMR (PMR II) was also appropriate because of increasing interest in the industry in this experimental but highly thermo-oxidatively stable matrix resin(3).

The program was divided into three basic tasks as described below.

Task I - Material Procurement and Acceptance

Three different PMR-15 prepreg materials were purchased from a commercial source; the three reinforcements were Thornel T-300 graphite fiber woven cloth, S-6581 woven glass cloth and unidirectional A-S Graphite fiber. Evaluations used to define lot characteristics included such tests as volatiles, resin solids content, resin flow, molded ply thickness checks, and elevated temperature flexure property determinations.

Task II - Composite Processing Studies

In this phase, four prepreg/process combinations with the first generation PMR (PMR-15) were investigated. Autoclave curing procedures utilizing low cost, locally heated tooling were developed for both glass and graphite cloth systems. Properties of die molded glass and A-S laminates were compared to the autoclaved cloth materials. Additionally, both S-6581 glass cloth and T-300 graphite fiber cloth were prepregged in-house with a second generation PMR polyimide. An autoclave cycle for PMR II was investigated and evaluated in the same manner as the purchased prepreg materials. Replicated determinations were conducted on both postcured and non-postcured laminates in flexure and shear at both room and elevated temperatures.

Task III - Development of Composite Data

Using the material/process combinations defined in Task II, property data collection included isothermal gravimetric analyses (ITGA) determinations at 260°C (500°F) and 316°C (600°F) for various time periods out to 2000 hours on both PMR matrix type composites. In addition to weight loss data, replicate shear and flexure determinations were conducted at planned intervals during the ITGA testing. Additional evaluations during this third phase of the program also included reverse bending fatigue at room temperature to determine endurance limits for the three material/process combinations with first generation PMR.

Experimental approaches, results, data interpretation and conclusions are described in the following sections.

2.0 PROGRAM MATERIALS

The following sections describe the basic program materials including purchased PMR-15 prepreg, PMR II monomers and reinforcements.

2.1 PMR-15 Vendor Prepreg

At the beginning of the program, three of the commercial reinforcement coaters in this country known to have the most extensive experience with the PMR-15 polyimide system were approached with a formal request for quotation to a specification defining the materials and quality requirements. On the bases of written responses and telephone communication, a single source was chosen to supply all three prepreg materials. This decision was reached on the basis of factors such as cost, completeness of response, reported monomer purity, and adherence to preparation techniques developed and published by both NASA and TRW on PMR technology.

U.S. Polymeric, Inc. of Santa Ana, California was the single source chosen to supply the needed prepregs. Appendix A delineates the purchase order requirements and specification provided to U.S. Polymeric for manufacture of the required materials. A deviation from the specification was requested by the vendor with regard to the tolerance limits on resin solids content. The vendor requested and was granted a tolerance of ±3% on resin solids content which represents standard commercial practice in the industry.

Further description of these materials is given below. Characterization of the prepreg materials is given in Section 3.0.

2.1.1 PMR-15 Resin

As was noted earlier, the PMR matrix system is prepared by combining three monomeric reactants in alcohol and then applying the solution directly to the reinforcing fiber for subsequent in situ polymerization, rather than employing a previously prepared prepolymer varnish. The monomers employed and the chemistry involved in curing are shown in figure 1.

A range of formulated molecular weight (FMW) materials can be used; the PMR-15 was chosen because of its excellent balance of properties. It is now common practice to designate the specific FMW system being discussed by eliminating the last two zeros from the FMW value and appending the remaining two digits to the PMR abbreviation. For example, a PMR system of a 1500 FMW becomes PMR-15. This convention is followed throughout this report.

The PMR-15 is formulated as shown below.

FMW	Moles of BTDE	Moles of MDA	Moles of NE
1500	2.084	3.084	2.000

The number of moles of the monomeric reactants in each of the monomeric solutions was governed by the following ratio:

$$n : (n + 1) : 2$$

where n, (n + 1) and 2 are the number of moles of BTDE, MDA and NE, respectively. The formulated molecular weight (FMW) is considered to be the average molecular weight of the imidized prepolymer that could have been formed if amide-acid prepolymer had been synthesized. The equation for FMW is:

$$\begin{aligned} FMW = {} & n\,MW_{BTDE} + (n + 1)\,MW_{MDA} \\ & + 2\,MW_{NE} - 2\,(n + 1)\left[MW_{H_2O} + MW_{CH_3OH}\right] \end{aligned}$$

where MW_{BTDE}, MW_{MDA}, etc. are the molecular weights of the indicated reactants and by-products(4).

2.1.2 Unidirectional Graphite Fiber Prepreg

The unidirectional graphite reinforcement chosen was A-S, a 10,000 filament tow from Hercules, Incorporated. The fiber is treated to enhance shear strength and has an advertised minimum tensile strength of 2.83 GPa (410 ksi) and a modulus of 221 to 248 GPa (32 to 36 msi).

The prepreg was manufactured by the vendor in a continuous tape form. Two lots of this material were received, the first in sheets as shown in Appendix A and the second lot in a roll with a width of 31 cm (12 inches). The first lot was rejected because of molding behavior; the second lot was used throughout the program. Details concerning the rejection are described in section 3.0.

2.1.3 Woven Graphite Fiber Prepreg

Union Carbide's T-300 fiber, in the form of 3000 filament yarn, was the material selected for use in woven cloth. While Appendix A shows only one type of T-300 cloth, two types of T-300 prepreg were, in fact, obtained and evaluated. The first was prepreg with the Union Carbide epoxy compatible size (UC-309); this material is identified, in this report, as T-300 (S). The other prepreg used a 23 x 24 inch weave cloth with the size removed by heat cleaning in air at 371°C (700°F) for one hour prior to resin application. This material is designated T-300 (HC). All other requirements were as shown in the Appendix.

2.1.4 Woven S-Glass Fiber Prepreg

The S-Glass reinforcement for the program prepreg was obtained from Burlington in a 181 weave with 57 warp ends/inch and 54 woof ends/inch. The filament is described as a SCG-150-1/2. The cloth carries a designation of S-6581. The cloth finish was a Burlington I-599 which was originally a development product identified as GB-855. The I-599 designation has subsequently been changed by Burlington to I-621.

2.2 PMR II Prepreg

The second generation PMR resin, PMR II, employs the same reaction chemistry of PMR-15, but two of the three monomers are different from the PMR-15 system. Figure 2 illustrates the monomers in the PMR II system. The paragraphs below describe the monomers and the reinforcements used in preparing in-house prepreg.

2.2.1 PMR II Matrix System

Based on previous work with PMR II(3)(5), it was planned to use ethyl esters and an $n = 1.67$, i.e., a formulated molecular weight of 1262. The stoichiometries of the three monomeric reactants to be used (figure 2) in this case are $n/(n+1)/2$, where n = moles of HFDE, $n+1$ = moles of PPDA, and 2 = the moles of NE.

The para-phenylenediamine (PPDA) and the diethylester of 4,4'-(hexafluoroisopropylidene)-bis (phthalic acid) (HFDE) were purchased (from duPont) in solution in ethyl alcohol; this system is designated NR-050X by duPont. The 5-norbornene-2, 3-dicarboxylic anhydride was purchased from Fisher Scientific Company and had a melting point range of 2°C (3.6°F). Anhydrous 200 proof ethyl alcohol for esterifying the norbornene anhydride was purchased from Publicker Industries, Inc.

Because of process difficulties encountered with the duPont NR-050X, described in section 3.2 below, PMR II composites based upon freshly prepared monomer solutions were also investigated.

The norbornene anhydride (2°C (3.6°F) mp range) compound was obtained from Fisher Scientific and esterified prior to use. The crystalline p-phenylenediamine (Certified Reagent Grade) with a 1°C (1.8°F) mp range was obtained from Fisher. The HFDE was purchased from Burdick & Jackson Laboratories, Muskegon, Michigan, in the anhydride form (HFDA). Burdick & Jackson separated HFDA from the duPont NR-050X using the procedure described in reference (5). Figure 3 shows a copy of the certification from Burdick & Jackson giving an infra-red spectrum and a melting point range of 1.5°C (2.7°F) on the 4,4'-(hexafluoroisopropylidene)-bis (phthalic anhydride).

2.2.2 PMR II Reinforcements

The woven fabric reinforcements were used in evaluating the PMR II; S-6581 and T-300 cloth. The S-6581 was as described in section 2.1.4 with the I-621 finish from Burlington. The T-300 was the 24 x 24 inch weave, described in section 2.1.3, with the Union Carbide finish.

Only the S-6581/PMR II was carried throughout the program; the T-300/PMR II was only taken through Task II, the process development studies. Details of monomer preparation, prepregging and process development are given below.

3.0 PREPREG CHARACTERIZATION

The following sections describe the procedures employed to determine the acceptability of the purchased PMR-15 prepregs and to prepare PMR II prepregs as well as static mechanical properties of these materials.

3.1 Purchased PMR-15 Prepregs

One lot of S-6581 reinforced prepreg was received, two lots of T-300 material (one with finish on the cloth and one without), and two lots of A-S material. With the exception of the first lot of A-S prepreg, all material was accepted and used throughout the program. Details of these efforts are discussed in the following paragraphs.

A first step was a determination of resin and volatile contents. Table I lists volatile contents and cured resin solids on each of the materials. As can be seen, the TRW determinations of resin solids indicate that all materials are high in resin content when compared to the established specification limits. The certification data from U.S. Polymeric, with the exception of the T-300 (S), also report high resin solids values.

It was determined that the high resin solids values resulted from a misunderstanding by the prepreg vendor; they used a total volatile content (determined at $316^{\circ}C$ ($600^{\circ}F$)) to adjust resin pick-up on the reinforcement. By using this method, the value determined included an imidization loss (17.1% of total monomer weight) which was not allowed for in the resin pick-up calculations. As a result of this error, all of their values were higher than planned. TRW resins solids contents were determined on cured laminates, molded under conditions to yield an insignificant amount of flow. Graphite fiber laminate samples were digested with sulfuric acid and hydrogen peroxide to determine resin solids and the glass laminate resin contents were determined by burn-off at $566^{\circ}C$ ($1050^{\circ}F$). Despite the high resin content values, it was decided to accept the deviated material to avoid further delay to the program.

3.1.1 A-S/PMR-15 Prepreg

Laminates were molded from all the prepreg systems received. Initial molding trials with the first lot of A-S/PMR-15 material revealed imperfections on the laminate surfaces. Further 10.2 x 10.2 cm laminates were prepared using molding pressures of 1.4 MPa, 3.5 MPa, 4.8 MPa and 6.9 MPa (200 psi, 500 psi, 685 psi and 1000 psi). Imidizing conditions were varied, including three hours at 121°C (250°F), one hour at 204°C (400°F) and two hours at 204°C (400°F). All of these laminates displayed the same surface conditions in greater or lesser amounts, with the low pressure molding, low temperature imidization conditions producing the greatest density of imperfections. Figure 4 is a photograph (1.7 magnification) of a 10.2 x 10.2 cm laminate showing the type of surface depressions encountered.

U.S. Polymeric referred to another organization that had used their A-S prepreg without encountering this problem. A sample of this five month old material was obtained and compared with the newly received prepreg. Ten ply laminates of each material were prepared by imidizing at 121°C (250°F) in the same oven at the same time. The laminates were molded in the same die in successive cycles employing the preform insertion at 232°C (450°F) and a pressure of 3.5 MPa (500 psi). The newly received material exhibited the same type of surface impressions observed on all the laminates fabricated while the older material, obtained from the outside organization, displayed a smooth surface free of any defects.

One laminate prepared from the new material (No. 772-5) was imidized for two hours at 204°C (400°F) and molded under 6.9 MPa (1000 psi) pressure at 316°C (600°F) for one hour. Triplicate flexure specimens tested at 316°C (600°F) showed an average strength of 585 MPa (84.9 ksi) and a modulus of 56 GPa (8.1 msi). These values are substantially below what might be expected even though the laminate was not postcured. The conclusion from these experiments was that some deficiency existed with the specific resin monomer solution or process parameters employed in manufacturing the program lot of A-S prepreg.

This first lot of A-S/PMR-15 prepreg was rejected, based on the surface defects described. The vendor agreed to replace the material at no additional cost. Discussions were held with the vendor to attempt to identify the problem. It should be noted that the process used to manufacture the unidirectional continuous fiber prepreg was different from that used with the woven cloth reinforcements, but what potential effect this might have was not clear. The type of defect observed with the A-S material was last seen on a previous program(6) in which the problem was ultimately identified as resulting from tri- or tetra-esters in the benzophenone ester-acid component of the monomer mix. Reference 7 discusses this in detail. To preclude this problem, it was agreed that the vendor would limit to three days each the time period between (a) esterifying the benzophenone component and mixing with the other monomers and (b) applying the mixed monomers to the reinforcement.

The replacement shipment of the A-S/PMR-15 prepreg from U.S. Polymeric was received in a continuous roll, 30.5 cm (12 inches) wide. The appearance of the prepreg was good. Fiber collimation, tack, drape and separation from the release paper were all excellent. U.S. Polymeric reported success with molding and excellent mechanical properties at both room and 316°C (600°F). TRW found a total volatile content of 11.0% and a cured resin solids value of 39.1 w/o vs. the reported value of 37.7 w/o; these values were judged acceptable.

There was concern about the potential quality of the molded appearance of panels due to the difficulties experienced with surface defects on the first lot received from U.S. Polymeric. For this reason, a number of laminates were molded with different cycles; the resin flow and quality results are shown in table II. Note that, while certain cycles produced some surface defects, these were much reduced in intensity from the first lot and, secondly, one cycle, with an imidization of one hour at 204°C (400°F) and 6.9 MPa (1000 psi) molding pressure, yielded defect-free surfaces. Photomicrographs and specific gravity determinations were used to determine that the laminates were essentially void-free.

Before making the final decision to accept the material, a laminate was molded (772-47) using the least likely cycle shown in table II; i.e., the one with a three hour imidize at 121°C (250°F), and tested at 316°C (600°F) in short beam shear and flexure. The results can be seen in table III. It was felt that these values reflected expected strength levels and the A-S/PMR-15 prepreg was accepted.

3.1.2 T-300 and S-6581 Prepreg

Multiple 10.2 x 10.2 cm (4 x 4 inch) laminates of both T-300 and S-6581 prepreg materials were molded to determine flow and to provide 316°C (600°F) flexure specimens, samples for resin solids and microscopic examination. Owing to the difficulty experienced with the A-S prepreg, it was felt necessary to mold more than one laminate from each material, using alternate cycles, to observe performance. Table IV displays the values determined for flow, specific gravity and thickness per ply on these laminates.

It is significant to note that, while the T-300 laminates molded with the standard 232°C (450°F) insertion temperature cycle did not yield clear resin flash, visual observation showed good consolidation and resin rich edges with the lower molding pressures and extruded resin with fiber wash at the higher pressures. It was not possible to obtain gel times due to the high viscosity of the extruded resin. Visual examination and photomicrographs revealed sound laminates of the T-300 materials as well as the S-6581 system.

Table V shows the results of flexure testing of several of the laminates discussed above. These unpostcured specimens were put directly into the 316°C (600°F) preheated Instron oven; no blistering was apparent on any of the specimens. Specimen failures were predominantly thermoplastic in nature with the appearance of ply buckling on the compressive side of the specimens. Despite this severe test cycle, it can be seen that the values reflect sound laminates representative of what would be expected of materials of these types. The one exception is the T-300 laminate 772-12; it is not known why this laminate displayed such low values. The repeat of this laminate, 772-15, produced strength values more appropriate for this material and in line with other data collected.

3.1.3 PMR-15 Prepreg Storage Life

Both the T-300 and the S-6581 were manufactured on October 20, 1976. The material was shipped in dry ice to TRW and put in storage. The T-300 was kept at -18°C (0°F); the S-6581 was kept at 4°C (40°F). On October 19, 1977 panels of both materials were die molded and inspected ultrasonically for voids. The materials still had ample tack and drape. The mold cycle of the 21.6 cm x 21.6 cm x 2.3 mm (8½ x 8½ x 0.090 inch) panels was as follows:

a) Oven imidize one hour at 204°C (400°F).

b) Insert in preheated die at 232°C (450°F) and hold at contact pressure.

c) Apply 6.9 MPa (1000 psi) and raise to 316°F (600°F) over a 20 minute period.

d) Hold one hour at 316°C (600°F).

The panels were submitted non-postcured for ultrasonic inspection. Both panels showed clear C-scans, indicating essentially void-free composites using the same standards applied throughout the program. While 6.9 MPa (1000 psi) was used vs. 1.4 MPa (200 psi) as in autoclaving, it seems safe to conclude that, after a one year storage period, no deleterious monomer effects occurred which interfered with the fabrication of sound composites.

The roll of A-S material, manufactured on February 17, 1977 and stored at 4°C (40°F), was found, in October of 1977, to have experienced blocking; i.e., the face of the prepreg fused to the back of the adjacent layer of the non-release treated side of the spearator paper. This condition prohibited further use of the material.

3.2 PMR II Prepreg Preparation and Characterization

First trials with the PMR II prepregging were conducted using duPont's NR-050X (Lot-144) which contains both PPDA and HFDE monomers. The first step in preparing the monomer solution was to reflux the norbornene anhydride in ethyl alcohol to prepare the monoethyl ester in a 79.5 w/o concentration. A reflux time of three hours was used to obtain complete reaction. To confirm the completion of this reaction, three infra-red spectrograms were prepared. Figure 5 illustrates the spectrogram of the norbornene anhydride as received; the circled peak at a wave number of 1770 was chosen as a characteristic one to be monitored in subsequent analyses. Figure 6 shows the spectrogram obtained when excess anhydride was deliberately mixed with the fully esterified norbornene ester-acid solution; the presence of the characteristic peak can still be clearly seen. Figure 7 is the spectrogram from the fully esterified material. As can be seen, only a "shoulder" remains at the 1770 wave number. This was taken as an indication that the esterification was complete and that the monomer solution was ready for blending with the other monomers.

The NR-050X solution was generally received in a precipitated condition. In order to put this material back in solution, mild heating was required. This was done by transferring the NR-050X material from the polyethylene bottle received from duPont to a resin kettle by rinsing with absolute methanol. The quart bottle contained approximately 1000 gm of the NR-050X and 200 grams of methanol were used. This technique achieved a quantitative transfer of the precipitated NR-050X to laboratory glassware. The resin kettle was fitted with a refluxing head and the monomer mix brought to refluxing temperature for just a moment and cooled immediately. Observation indicated that the material went into solution more quickly and remained in solution longer with the use of the methanol when compared to straight ethanol solvent used in previous trials. At this point, the norbornene ester solution was added. Done in this way, the final monomer mix yielded a cured resin solids content of 41.7 w/o.

Both T-300 and S-6581 prepreg were prepared with the PMR II solution by spreading the required amount of solution onto a pre-weighed section of cloth. Inspection of the S-6581 material against a back-light showed an even, uniform coating of the PMR II. Staging trials clearly revealed the prolonged tack life and volatile retention experienced with the ethyl alcohol carrier solvent as compared to the PMR-15 with methyl alcohol.

Both die and autoclave molding with this material revealed much higher flow behavior than anticipated, based on the similarity of the curing mechanism to PMR-15. First autoclave cycles revealed blisters using a standard process. An extensive series of experiments was performed to develop a processing cycle suitable for this material. Ultimately, sound test panels were produced with reasonable flow levels by two methods; one cycle included a 60 minute hold at 260°C (500°F) before pressure application and the other required that the laminate be wrapped in porous

TFE coated glass cloth and then a non-porous TFE coated glass cloth to mechanically restrict resin expulsion.

While the experiments described above were in progress, a second quantity (Lot -30) of the NR-050X was obtained and investigations initiated on this new lot and an earlier sample lot (Lot -87) obtained for internal programs. Both of these lots exhibited similar behavior, quite different from the high flow lot (Lot -144), more in line with the expected processing performance. Flow quantity and time of occurrence during the standard die and autoclave cycles were very like PMR-15. Based on these tests, it was decided that the initial batch of NR-050X was anomalous and that all further work should be done with the second lot received.

Trial laminates, using a standard autoclave cycle, were prepared; ultrasonic inspection indicated that these panels were sound. These panels were then postcured and submitted for mechanical tests at 316°C (600°F). As can be seen from table VI, these values confirm the acceptability of the -30 replacement lot of NR-050X. This material was used throughout Task II.

Difficulties in prepregging with the NR-050X included precipitation and variation of color, consistency, appearance and mixing response from batch to batch and quart to quart within a lot. These problems prompted the investigation of freshly prepared PMR II solutions. For reasons of superior solvency and economy, it was decided to use methyl alcohol as a carrier solvent and methyl esters in the monomer preparation.

The complete PMR II monomer solution was prepared by separately esterifying the two anhydride compounds in methyl alcohol to yield 50 w/o solutions of the methyl esters and mixing these two materials. The norbornene compound was esterified as described above. The HFDA was refluxed for two hours to complete esterification. The PPDA compound is insoluble in room temperature alcohol; it was added to the mixed esters with enough methyl alcohol wash to represent a 50 w/o mixture. When added in this manner, the PPDA dissolved almost immediately, yielding a complete 50 w/o monomer solution with no residual undissolved material. A solution of this concentration represents a cured resin solids content of 41.2 w/o.

This monomer solution was spread evenly on pre-weighed S-6581 glass cloth and dried overnight at room temperature. Ten plies of this first prepreg were stacked, oven imidized at 204°C (400°F) and die molded at 6.9 MPa (1000 psi). Resin flow was 4.6 w/o and the laminate appeared quite sound. In fact, the 1.8 mm (0.070 inch) laminate was translucent when held up to a fluorescent room lighting fixture.

A second laminate was molded from this same prepreg in the same way except using 3.4 MPa (500 psi) pressure; this laminate yielded less than 1% flow. The panel was postcured at 316°C (600°F) and tested in flexure and shear; results are shown in table VII. The mechanical properties clearly indicate a high quality laminate.

Storage of the complete solution at room temperature for an eight-hour period showed no perceptible change. Some solutions were kept longer than this without precipitation; however, one batch did precipitate overnight and was used to prepare an experimental prepreg. This prepreg molded without difficulty in the same manner as the unprecipitated material and yielded a sound laminate. However, this practice is not recommended because of potential loss of reproducibility.

Once the monomers have been applied to the reinforcement, the prepreg may be held for some time prior to molding. Samples of PMR II prepreg of both T-300 and S-6581 were held for approximately two months in 4°C (40°F) storage and molded at 6.9 MPa (1000 psi) in a die as described in paragraph 3.1.3. Both panels (21.6 cm x 21.6 cm x 2.3 mm) were inspected ultrasonically. The S-6581 panel showed no sonic indications, while the T-300 panel exhibited indications at each of the four corners of about 3 cm^2 in size. While no microscopic sections were taken of these defect areas, it seems clear the PMR II prepregs do have significant storage life at 4°C (40°F).

Because of the uniform, excellent handling and good properties obtained, this approach, i.e., the use of individual monomers, was used throughout Task III efforts.

4.0 COMPOSITE PROCESSING STUDIES

Task II was centered on developing processing cycles for the die and autoclave molding of both PMR-15 and PMR II prepregs. The specific material/process combinations studied included:

PMR-15/A-S	Die Molded
PMR-15/S-6581	" "
PMR-15/S-6581	Autoclave Molded
PMR-15/T-300	" "
PMR II/S-6581	" "
PMR II/T-300	" "

Laminate evaluation consisted of room temperature and elevated mechanical properties both before and after postcure.

4.1 PMR-15 Die Molded Process Development

Based on previous experience, the molding of small laminates for materials of small test laminates, it was decided that a molding pressure of 3.4 MPa (500 psi) was adequate when used on S-6581 prepreg that had been imidized at 121°C (250°F) for three hours.

Three large panels of the S-6581 glass cloth/PMR-15 were then fabricated in a closed die. The warp oriented laminates were 10 plies thick by 21.6 x 21.6 cm (8.5 x 8.5 inches). The prepreg stacks were oven imidized for three hours at 121°C (250°F) prior to insertion in a preheated die at 232°C (450°F). They were held at this temperature for 10 minutes under contact pressure, after which the pressure was increased to 3.4 MPa (500 psi) and the temperature brought to 316°C (600°F) in a 20 minute period. After reaching 316°C, the parts were held for one hour before cooling.

The panels were then cut in half and one half of each panel postcured at 343°C (650°F). Postcure was accomplished by sandwiching the panels between glass fabric with a light weight on top; the 343°C (650°F) temperature was achieved in a four-hour period and the parts held at this temperature overnight (16 hours). Table VIII lists the weight losses experienced in postcure as well as the resin flow observed during fabrication, laminate thicknesses and densities. All panel halves were submitted for ultrasonic examination. The laminates were inspected at 5 MHz using varying sensitivities. A review of these C-scans led to the choice of laminate number 772-30 for further evaluation. These panel halves, as-molded and postcured, were machined into specimens for short beam shear and flexure testing, resin content by burn-off, and microscopic examination.

As noted in table VIII, the specific gravity of 772-30 was 1.90. Using this value and the resin solids (33.5 w/o) for this panel, the void content was calculated to be 0.3 v/o. The microscope specimens, chosen from the C-scan at various points, were used to establish standards for subsequent ultrasonic tests.

Mechanical test data collected are shown in tables IX and X. A review of the data in these tables shows that the non-postcured room temperature values are equivalent to those seen in the industry with similar laminates using the best epoxy matrices. Postcure can be seen to reduce room temperature performance but provides improved resistance to the elevated temperature environment. This behavior has been observed with high strength graphite reinforcements and was not unexpected. In general, it is felt that these properties reflect high quality laminates and an excellent combination of matrix and reinforcement.

As was noted above, the second shipment of A-S/PMR-15 prepreg was accepted and a cycle chosen for die molding. Using this cycle, three panels 21.6 x 21.6 cm (8.5 x 8.5 inches) were molded. The cycle used included a one hour oven imidization at 204°C (400°F), insertion into a preheated die at 232°C (450°F) with a 10 minute hold, the application of 6.9 MPa (1000 psi) pressure, and an increase to 316°C (600°F) in 20 minutes; half of each of the panels was postcured at 343°C (650°F) for 16 hours. The characteristics for each of the panels molded are shown in table VIII. Ultrasonic C-scans and photomicrographs were used to determine that the panels were void free. No change in ultrasonic response was noted after the 16 hour postcure.

The mechanical test results from the selected panel, 772-50, in both postcured and nonpostcured condition are shown in tables XI and XII. It is felt that the values obtained reflect a sound laminate and are representative of the fiber volume and reinforcement type.

4.2 PMR-15 Autoclave Molded Process Development

In anticipation of the autoclave development portion of the program, considerable thought had been given to a suitable vacuum bag-tool arrangement. Figure 8 shows a schematic of the concept selected, employing electrically heated blankets and a cured silicone rubber bag, sealed by a silicone rubber O-ring. The use of the locally heated tool would permit the attainiment of the 316°C (600°F) cure temperature at a controlled heating rate, and provide a system in which only the tool had to be heated instead of the entire autoclave volume. It was felt that the O-ring mechanism would be positive and permit rapid assembly and removal. It was hoped that multiple uses of the bag and O-ring could be obtained. Autoclave dry runs (without prepreg material present) were made to determine the temperature resistance of the silicone rubber bag and O-ring and to confirm the operation of the autoclave temperature and pressure systems. The system operated as planned.

Since all autoclave systems seemed suitable, a first trial run was attempted using a 10.2 cm x 10.2 cm laminate, each of PMR-15/T-300 (sized) and the PMR-15/S-6581 glass prepregs. The unimidized prepreg stacks were placed on the tool, subjected to a vacuum of about 75 mm of Hg and the temperature brought to 316°C (600°F) as shown in the curve plotted in figure 9. Twenty-seven minutes after turning on the heat, the mandrel had achieved a temperature of 246°C (475°F) and full vacuum was applied and the autoclave pressurized. As can be seen from the curve, 10 minutes later a pressure of 1.3 MPa (195 psi) was attained. A sharp jump in temperature at about 160 minutes can be seen on the curve in figure 9. It was noted during the course of this run that the maximum temperature obtainable was 302°C (575°F) at the full autoclave pressure. It was assumed that a thermal balance was achieved between heat input and that dispersed to the interior of the autoclave. By reducing the autoclave air pressure to 0.7 MPa (100 psi), the temperature climbed to 316°C (600°F) without any change in temperature controller settings. This was apparently due to the reduced conduction of heat in the less dense air.

These two trial parts appeared sound when visually examined. Ultrasonic C-scans were obtained on both laminates. Based on the C-scans, specific gravity measurements and microscopic examination, both of these laminates were determined to be sound and essentially void free.

The problem of attaining 316°C (600°F) was subsequently resolved by changing from the steel tool used during this run to a slightly smaller aluminum tool. The steel tool was 13 mm (0.5 inches) thick, with the other dimensions being 30.5 x 61.0 cm (12 x 24 inches). The aluminum tool was 9.5 mm thick by 28.6 x 61.0 cm (11-1/4 x 24 inches). The larger steel tool provided excess stock not needed for vacuum sealing which acted as a cooling fin. By going to the narrower tool, this fin was eliminated and the required 316°C (600°F) maximum temperature was thereafter easily reached.

Figures 10 through 12 shown photographs of the assembly of the autoclave bagging system with the heated blankets. While the system, as shown, was successful, minor changes were made subsequently to improve convenience and lower cost. For instance, it was determined that a maximum of three runs could be made with the silicone rubber (Cohrlastic 500) bag and O-ring after which difficulty was encountered. The silicone rubber bag was discarded in favor of duPont Kapton film, which was replaced with each run.

Two other approaches were tried for the outer seal: (1) the use of a conventional sealing type method employing an A800 material (Airtech International, Inc., Torrance, California) good to 427°C (800°F), and (2) the use of a pair of flat silicone rubber gaskets to replace the O-ring and the lower sealing frame. This later technique proved to be quite suitable and was used throughout the remainder of the program.

Using the system as just described, a number of 20 x 20 cm laminates of both the PMR-15/S-6581 and the PMR-15/T-300 material were manufactured. In each case, unimidized material was stacked on the tool and bagged in the manner described above. The cycle employed is shown graphically in figure 13.

All of the laminates appeared sound and well consolidated. Using laminate specific gravity values and the resin solids values determined on the incoming prepreg, the void contents on the three S-6581 laminates were 0.5 v/o. In the case of the T-300 laminates, two autoclave runs were made with paired laminates of sized and heat cleaned material. These composite specific gravities indicate a void content of 0 to 2.6 v/o on the sized T-300 and 1.3 v/o on the heat cleaned cloth laminates. Table XIII lists the characteristics for these laminates. As can be seen from the specific gravity values, uniformity among multiple runs was good. Photomicrographs and ultrasonic C-scans, with few exceptions, indicated essentially void-free composites.

One panel was sectioned from the three fabricated of each material and half postcured. For each material, both the postcured and unpostcured halves were machined into specimens for triplicate testing of short beam shear and flexure at room temperature and 316°C (600°F). The results for the autoclaved PMR-15/S-6581 material are shown in tables XIV and XV. Note that, in addition to the selected panel (772-36) which was molded with a caul plate on top of the laminate, postcured laminate data for 772-35 molded without a caul plate are included. While the short beam shear values are comparable for the two laminates in the postcured condition, the flexure values for the laminate molded without the caul plate (with the bleeder imprinted surface) are significantly lower in flexure strength.

In considering the values for panel 772-36, there seems to be a significant drop in room temperature shear strength from nonpostcured to postcured, but, in general, the values seem quite good. With regard to an important characteristic, strength at 316°C (600°F), the postcured autoclave panel values compare very well with the postcured die molded values obtained with this same prepreg lot reported previously and summarized below:

	Flex Strength	Short Beam Shear Strength
Autoclave Molded, MPa	447 (64.8 ksi)	34 (5.0 ksi)
Die Molded, MPa	440 (63.8 ksi)	35 (5.1 ksi)

Tables XVI and XVII show all the data collected on the autoclaved T-300/PMR-15, including both the sized and heat cleaned T-300 prepregs. Little can be said about the absolute levels of the values, except that they reflect what the reinforcement is capable of providing, indicating sound laminates. Strength retention at 316°C (600°F) seems quite good. Little difference can be seen between the sized or heat cleaned reinforcement. However, the sized material exhibits slightly better strength retention when comparing the high temperature performance of the postcured laminates. For this reason, it was decided to conduct the remainder of the program with the sized T-300 material.

4.3 PMR II Process Development

As was noted in Section 3.2, considerable effort was expended in establishing process parameters for the PMR II material. Tables VI and VII show autoclave and die molded properties, respectively, on S-6581 glass cloth. Using this experience and the autoclave cycle developed for PMR-15 (figure 13), both S-6581 and T-300 cloth prepregs were prepared using the NR-050X base. Three 20 x 20 cm panels of each material were autoclave molded, cut into two sections and half of each laminate postcured at 343°C (650°F). Target resin solids contents of 35 and 40 w/o (equivalent to the PMR-15 materials evaluated) were achieved for the S-6581 and T-300, respectively. The T-300 cloth had the UC 309 finish applied by Union Carbide and the S-6581 glass cloth had the Burlington I-621 polyimide compatible finish.

Ultrasonic inspection and microscopic examination indicated that the composites were essentially void free. Specific gravities of the selected panels were 1.94 for the S-6581 and 1.58 for the T-300; slightly higher than comparable PMR-15 laminates due to the higher specific gravity of the fluorine bearing resin. Thicknesses of the laminates were 2.0 mm, giving a per ply thickness of 0.23 mm (9.1 mils) for the S-6581 and 0.43 mm (16.8 mils) for the T-300 cloth.

Laminate flexure and short beam shear specimens were machined from both nonpostcured and postcured halves tested and at 316°C (600°F). All the data collected are shown in tables XVIII and XIX. A review of the test values indicates that, in general, the strength and modulus levels compare well with PMR-15. However, the high temperature shear and flexure values of the PMR II in the non-postcured condition are much higher than those realized with PMR-15 on either reinforcement in the non-postcured condition and are equivalent to the postcured PMR II laminate halves. From these results, it can be concluded that the PMR II matrix system is suitable for use at 316°C (600°F), at least in the short term, without the need for postcure.

5.0 DEVELOPMENT OF COMPOSITE DATA

Using the processing techniques developed in the previous taks, a series of laminates were prepared, inspected and evaluated for fatigue characteristics in bending, thermo-oxidative stability by isothermal gravimetric analysis (ITGA), and residual strength dterminations. The following sections describe procedures, test methods and results.

5.1 Isothermal Gravimetric Analysis of PMR Laminates

A series of six different material/process combinations were examined with this technique. Those evaluated, and the temperatures employed, are shown below:

Resin	Reinforcement	Fabrication Process	Evaluation Temperature	Exposure Time
PMR-15	T-300(S)	Autoclave Molded	260°C (500°F)	1000 hr
	A-S	Die		1000 hr
	S-6581	Autoclave	↓	2000 hr
		Autoclave	316°C (600°F)	
↓		Die		
PMR-II	↓	Autoclave ↓	↓	↓

Multiple laminates of each kind, shown in the table above, were prepared using the procedures described in the preceding sections. All laminates were ultrasonically inspected after postcure at 316°C (600°F). Those selected for use were determined to be essentially void free; this was confirmed by photomicrographs. Additionally, triplicate analyses for resin content were conducted. All laminates were approximately 20 cm x 20 cm x 2.3 mm (8 x 8 x 0.090 inches). These were cut into plaques approximately 5 cm x 20 cm for use as samples in the exposure ovens. The plaques were withdrawn at the pre-selected intervals and machined into mechanical test specimens.

The test plaques were supported in stainless steel wire racks and placed in a closed inner oven chamber (see figure 14). This inner chamber, with a volume of 14 liters, was fitted with a coiled metal tube, fitted on the bottom of the chamber, with small holes drilled on 2.5 cm centers through which air was metered from a compressed air tank. A flow rate of 100 ml/min was maintained with calibrated flowmeters. The compressed air was hospital grade with a dew point temperature of -59°C (-75°F). Temperature inside the chamber was monitored with a calibrated thermocouple during the entire test and oven temperature adjusted to yield the target temperature.

5.2 ITGA Test Results and Discussion

Weight loss data from the 260°C (500°F) exposures are shown in tabular form in table XX; these data are plotted in figure 15. Retention of flexure strength, modulus and short beam shear strength is shown in tables XXI through XXIII. As can be seen from a review of the data, both strength and weight losses are moderate. No particular comparative trends among the three materials evaluated at this temperature are apparent, although the performance of the glass reinforced material out to 2000 hours is quite good for this length of exposure.

The 316°C (600°F) ITGA data are presented in figure 16 and tables XXIV through XXVII. An examination of the data leads to the identification of two significant observations: a) superior performance of the PMR II matrix system and b) equivalent performance of the die and autoclave molded S-6581 composites.

Both the tabular data and the curves in figure 16 show that the weight loss of the PMR II system is markedly lower than the PMR-15 material. Additionally, the PMR II curve seems to be leveling out at 2000 hours, rather than showing the sharp decline of the PMR-15 composites. The superior performance of the PMR II materials is also borne out by retention of flexure and shear strength out to 2000 hours, whereas the PMR-15 laminates were too degraded to warrant testing after 1000 hour exposures.

The weight loss and mechanical property test values of the PMR-15/S-6581 laminates prepared by die and autoclave molding can be seen to coincide within the limits of experimental error. It is felt that this confirms the high quality of the autoclaved panels and establishes the fact that the PMR-15 system can be successfully autoclave molded at a pressure of 1.4 MPa (200 psi).

Another trend observed in the 316°C (600°F) ITGA data in general is that the percentage weight loss and property retention of the S-glass reinforced PMR-15 composites seems markedly inferior to values previously reported(1)(6) with the

PMR-15 matrix system on HM-S high modulus graphite reinforcement. Control specimens of HM-S/PMR-15 were carried as a control in the 316°C (600°F) ITGA exposures (see table XXIV) conducted on this program and the weight loss of these specimens showed values reproducing those of references 1 and 6. It is therefore assumed that the more rapid degradation shown by the S-glass reinforcement composites is related to the effect of this type of reinforcement. Evidence of the degradation of the glass reinforcement is shown by the high loss of PMR II/S-glass mechanical properties at low levels of composite weight loss at 316°C (600°F) (see tables XXIV and XXVII). Because of the inert nature of the glass reinforcement, such an effect was not anticipated. No back-to-back performance comparisons between composites with these two reinforcements have been seen to confirm these observations. More work is needed to confirm the accelerated degradation effect and isolate the phenomenon before final judgments can be made.

5.3 Reverse Bending Fatigue

Limited fatigue data on the type of materials discussed in this program are available. The literature reviewed indicated that there are no data on composite performance determined in fully reversed bending fatigue in which both ends of the test specimens are supported. For these reasons, it was decided to collect such data on several types of the PMR-15 composites investigated.

5.3.1 Test Methods

The test equipment selected to perform the room temperature fatigue studies included a bending fatigue fixture from SATEC Systems (Grove City, Pa.) coupled with a Baldwin SF-1-U universal fatigue machine. The SATEC fixture (figure 17) clamps the test specimen on both ends and applies a uniform bending moment between the two loading pivots over the entire free length of the specimen. A dynamic alternating load is produced by a revolving eccentric mass giving a fully reversed bending cycle. Using this device, a given load is pre-set and then the motor speed is gradually brought up to produce a load application frequency of 1800 cycles per minutes. As the test continues, specimen degradation occurs with an accompanying increase in deflection but with the load at the same level. When the deflection becomes excessive, a microswitch is contacted, the machine is automatically shut down and a cycle counter is tripped, recording the elapsed number of cycles. One cycle is counted as one fully reversed excursion; i.e., top and bottom specimen surfaces each receive one tension and one compression exposure.

The standard SATEC fixture was modified in two ways: (a) the free specimen length between grips was reduced from 7.62 cm (3 inches) to 5.08 cm (2 inches) and (b) the minimum length between pivot points was reduced from 7.62 cm to 5.08 cm. This was done to limit specimen thickness anticipated owing to the significantly lower modulus realized with the composite materials compared to that of the metal specimens ordinarily run with the standard fixture design. The equations relating thickness to specimen stress, modulus and machine load were provided by SATEC and are shown in Appendix B.

Figure 18 shows the specimen design for use with the fixture. The reduced gage section shown is a requirement to induce failure away from the grips. Since a pure moment is induced into the specimen, the load is the same all along the free specimen length between the grips and, using a straight sided specimen, failure would invariably occur at the point where the grips contact and weaken the specimen. Also shown in figure 18 are the nominal thicknesses for each of the materials to be evaluated. Thicknesses were selected on the basis of material properties and machine load and deflection limitations as described in Appendix B.

First trial runs with the new fixture using program composite materials showed premature failures. Additionally, visual observation seemed to indicate that, on the rise to operating frequency during startup, some excessive deflection of the specimen was encountered due to secondary resonance modes in the fixture. To confirm this a specimen was fitted with strain gages and strain monitored during startup. This technique quickly revealed that, in fact, excessive deflection of the specimen was experienced; momentary excursions of this type could induce premature damage in the specimen, leading to failure at an accumulated cycle level less than anticipated.

To eliminate this excessive deflection phenomenon, a fixture damping technique was developed to inhibit deflection until the maximum cycling frequency

(1800 cycles/min.) was achieved. Multiple runs with the strain gage specimen, at various loading levels, demonstrated that the damping procedure was effective in eliminating these anomalous excursions and that a stable dynamic condition could be achieved by the use of the method.

Using the fixture damping technique, a number of PMR-15/T-300 cloth specimens were taken to failure at high loads to observe machine performance and failure locus. These preliminary runs established that the specimen design was appropriate and that the fixture was operating properly.

In order to establish base line flexure strength values for comparison with fatigue failure stresses, a series of four-point flexure tests were conducted on the program materials in both reduced and straight sided configurations on both "thick" (approximately 6 mm) and "thin" (approximately 2 mm) specimens. In testing the thick specimens, the inner span was set at the free specimen length (7.1 mm) of the fatigue fixture and the outer span adjusted to give a span-to-depth ratio in the range of that suggested by the ASTM method. The thin specimens were subsequently tested at approximately the same span-to-depth ratio. Tests were conducted on the Instron Tensile Testing Machine observing the usual standard practices. Beam width, in the case of the reduced gage section, was used in the calculations as the narrowest width.

5.3.2 Test Results and Discussion

Panels were fabricated of each of the materials to be evaluated in fatigue. Included were the following material/process combinations:

a)	A-S/PMR-15	Die Molded Unidirectional
b)	T-300 Cloth/PMR-15	Autoclave Molded
c)	S-6581 Cloth/PMR-15	Die Molded
d)	S-6581 Cloth/PMR-15	Autoclave Molded

All of the panels were fabricated using the processes developed in the first phases of the program and described above. It should be noted that the standard autoclave process was used without alteration to successfully mold panels 20 cm x 20 cm x 7.3 mm (8 x 8 x 0.288 inches). After postcure at 316°C (600°F) for 16 hours, panels were machined into flexure and fatigue specimens.

The results from the four-point flexure testing of program materials in both thickness and gage length configurations are shown in tables XXVIII and XXIX. No clearly significant trends can be observed in comparing the two thicknesses and gage configurations among the materials tested. There also appear to be no differences between the three-point flexure results reported earlier and the four-point data shown in these two tables. For this reason, the base line average for use in evaluating flexure fatigue performance was constructed by using both three-point flexure data and the values from four-point flexure tests with the straight sided gage sections. In the case of the S-6581 composites, both autoclaved and die molded laminate values were combined for a grand average. These baseline flexure values for the S-6581/PMR-15 and T-300/PMR-15 were 581 MPa (84.3 ksi) and 669 MPa (97.0 ksi), respectively.

Figures 19 and 20 show failed fatigue test specimens of S-6581 and T-300 reinforced composites. These represent typical failure modes observed for these materials. Note that the failure locus is within the gage section and is associated with the surface of the specimen. These were judged appropriate types of failure given the specimen design and loading mechanism applied.

Difficulty was encountered with the unidirectional A-S composites. Figure 21 displays the different specimen configurations evaluated with the unidirectional A-S/PMR-15 material. Three specimens employed a completely unidirectional layup; a straight sided specimen, one with a reduced gage section, and a tabbed specimen. The fourth specimen type was a cross-ply type with an outer surface angle ply. Failure modes observed included axial splitting, failure at the grips and, in the case of the tabbed specimen, excessive heat buildup at the bond line and adhesive degradation within minutes of test initiations. Figure 22 displays both the failure at the grips and cracks across plies at the edges of the specimen associated with the reduced gage section radius. Since all of these failure modes observed with the unidirectional A-S were considered to be unacceptable, further testing was discontinued.

Figures 23 through 25 show the S/N curves plotted from the fatigue data assembled. Table XXX is a summary of composite fatigue behavior at the ten million cycle mark. Figures 23 and 24 represent a further confirmation of the similar behavior of the autoclave and die molded S-6581/PMR-15 composites. As can be seen from table XXX, the ten million cycle stress levels are very similar, with the die molded specimen average showing a slightly higher value (11%) and a slightly narrower spread (17 MPa vs. 19 MPa). Figure 25, the S/N curve for T-300 reinforced PMR-15, shows the improved performance due to the carbon fiber reinforcement when compared to the glass cloth specimens. Table XXX shows a 1 x 10^7 cycle stress level of 29-38% vs. 11-16% for the glass reinforced materials.

The percent of ultimate stress level at 1 x 10^7 cycles for the materials tested did not deviate significantly from what might be expected. Harris(8), in discussing cyclic flexural tests of carbon fiber reinforced plastic (cfrp) indicates that, "They suggest that a realistic value for the fatigue strength at 1 x 10^6 cycles of cfrp in bending would be approximately 65% of the static strength for repeated bending in one direction and as low as 30% for fully reversed bending." The data in table XXX show a range of 29 to 38% of ultimate at 1 x 10^7 cycles for the T-300 reinforced composites tested. Mettes and Lockwood(9) report that an S-glass cloth/epoxy system showed a stress level of 20.0 to 22.5% of ultimate tensile strength after 1 x 10^7 flexure cycles. These flexure fatigue tests were run on a cantilevered specimen in accordance with the ASTM-STD-91 method for metallic materials. In general then, it seems that the reinforcement type and form played a larger role in fatigue performance than the matrix system.

A final test series consisted of an examination of retained four-point flexure strength after fatigue test. Table XXXI presents the data collected. As can be seen, with the exception of one S-6581 specimen, strength after fatigue testing at the stress and cycle levels shown is remarkably good.

6.0 PROGRAM CONCLUSIONS

Specific conclusions on such things as processing detail and material properties are presented in the body of the text. The conclusions below represent broader statements related to the program objectives and the more general characteristics of the PMR polyimide composite systems evaluated.

1) High quality PMR-15 prepreg with woven graphite or glass fiber reinforcement can be manufactured on a commercial basis and can be stored under refrigerated conditions for at least one year. Continuous graphite fiber/PMR-15 tape prepreg from the one vendor investigated was less than satisfactory in terms of reproducibility and indicates that further study of a prepregging process for this type of material is required.

2) PMR II prepreg can be prepared successfully from individual monomers or from a commercially available base containing two of the three monomers, although this latter approach (combined monomer base) is more involved and left a lack of confidence in reproducibility. The PMR II materials were found to process, both in a die and an autoclave, with the same ease and fabrication cycles as PMR-15 materials and were determined to have at least a two-month refrigerated storage life. It appears that the PMR II system does not require a postcure if used at a temperature of 316°C (600°F) or lower.

3) The use of the locally heated autoclave tool approach, as opposed to the convection heating of the complete inner volume of the autoclave, was demonstrated to be an energy-efficient, quick, controllable process. The process reproducibly produced high quality, essentially void-free PMR-15 and PMR II composites at 200 psi, on both glass and graphite cloth reinforcements, with equivalent properties to composites molded in a closed die at much higher pressures.

4) Isothermal gravimetric analysis at 316°C (600°F) and the subsequent mechanical test of exposed specimens clearly revealed the superior thermo-oxidative resistance of the PMR II matrix system over PMR-15 on the same reinforcement. Comparison of property retention and weight loss values of the PMR-15 and PMR II matrices on S-glass reinforcement to data previously collected with the PMR-15 on

high modulus graphite fiber reinforcement showed a highly accelerated degradation of the glass reinforcement materials, reflecting the need for further studies in this area.

5) Fatigue tests in a fixture which clamped both ends of the specimens were successfully conducted establishing a satisfactory specimen and the utility of the test method when used with woven cloth composites. The method was not suitable for unidirectionally oriented composites. The data demonstrated the influence of the reinforcement in composite fatigue performance and the nominal fatigue behavior of the PMR-15 matrix composites.

7.0 RECOMMENDATIONS FOR FURTHER WORK

1) The improved thermal performance of the PMR II system over the PMR 15 matrix, coupled with an equivalent ease of fabrication, points out the attractiveness of the material and the need for further data accumulation with the PMR II system; specifically, on other reinforcements, such as carbon and graphite fiber, and in alternate forms, e.g., molding compounds.

2) The discrepancy noted between the thermal performance of PMR-15 composites reinforced with graphite and glass indicates a strong need for further work in the area of defining the contribution of the reinforcement to composite thermo-oxidative stability and the mechanism of thermo-oxidative degradation of fiber reinforced composites.

3) The difficulties experienced with continuous graphite fiber prepreg highlights the importance of identifying or establishing appropriate prepregging methods.

TABLE I

U.S. POLYMERIC PREPREG RESIN AND VOLATILE CONTENTS

Material/Test	Specification	U.S. Polymeric Cert.	TRW Determined Values
A-S/PMR-15 (1st lot)			
Vol, %	11-15	11.8	10.3
Cured Solids, %	30.6-36.6	38.5	38.0
A-S/PMR-15 (2nd lot)			
Vol, %	11-15	16.0	11.0
Cured Solids, %	38.0(c)	37.7	39.1
T-300(a)/PMR-15			
Vol, %	11-15	12.3	13.2
Cured Solids, %	31.1-37.1	35.8	42.0
T-300(b)/PMR-15			
Vol, %	11-15	14.7	-
Cured Solids, %	31.1-37.1	40.0	40.2
S-6581/PMR-15			
Vol, %	11-15	10.3	9.4
Cured Solids, %	24.5-30.5	34.9	34.6

NOTES:
(a) Resin applied to cloth as received from weaving vendor.
(b) Woven cloth heat cleaned prior to resin application.
(c) Specification value was changed to correspond to other materials for comparison purposes.

TABLE II

10.2 x 10.2 cm A-S/PMR-15 ACCEPTANCE LAMINATES (SECOND LOT)

Laminate No.	Imidization Time/Temp.	Mold Pressure MPa (psi)	w/o Flow	Appearance
772-42	3 hr/121°C (250°F)	3.4 (500)	10.0	Some surface defects
772-44	1 hr/204°C (400°F)	3.4 (500)	No flash	Trace of defects
772-45	2 hr/204°C (400°F)	6.9 (1000)	No flash	Good
772-46	1 hr/204°C (400°F)	6.9 (1000)	2.0 Est.	No flaws
772-47	3 hr/121°C (250°F)	3.4 (500)	4.3	Few defects

NOTE: All panels were placed in a die preheated to 232°C (450°F) and held 10 minutes before pressure application and brought to 316°C (600°F).

TABLE III

MECHANICAL TEST RESULTS ON DIE MOLDED A-S/PMR-15 ACCEPTANCE LAMINATE

		316°C (600°F) Short Beam Shear		316°C (600°F) Flexure			
				Strength		Modulus	
		MPa	Ksi	MPa	Ksi	GPa	Msi
Panel 772-47		48	6.9				
As-Molded		47	6.8	765.3	111.0	84	12.2
		48	6.9	759.1	110.1	75	10.9
	Avg	48	6.9	762.6	110.6	80	11.6
Panel 772-47		59	8.6				
Postcured		58	8.4	1064	154.3	96	13.9
		60	8.7	1149	166.6	99	14.4
	Avg	59	8.6	1106	160.4	98	14.2

NOTE: Mold cycle: oven imidize 3 hours at 121°C (250°F), insert in preheated die 232°C (450°F), 3.4 MPa pressure, one hour at 316°C (600°F), 4.3 w/o flow. Postcured at 343°C (650°F) for 16 hours.

TABLE IV

MATERIAL ACCEPTANCE CHARACTERISTICS

Reinforcement	Lam. No.[a]	Imidization[b] Time/Temp. hr/°C (°F)	Mold Pressure MPa	Mold Pressure Psi	Flow %	Sp. Gr.	Thickness mm/ply (mils/ply)
T-300 (S)	772-6	1/204 (400)	1.4	200	0.1	1.52	0.396 (15.6)
	772-7	2/204 (400)	6.9	1000	0.0	-	0.381 (15.0)
	772-18	0/0[c]	1.4	200	1.6	-	0.396 (15.6)
	772-19[d]	2/204 (400)	1.4	200	0.9	-	0.401 (15.8)
T-300 (HC)	772-11	1/204 (400)	6.9	1000	0.0	1.56	-
	772-12	1/204 (400)	1.4	200	0.0	1.53	0.396 (15.6)
	772-15	1/204 (400)	1.4	200	0.0	-	0.384 (15.1)
S-6581	772-20	1/204 (400)	1.4	200	0.5	1.88	0.226 (8.9)
S-6581	772-24	1/204 (400)	6.9	1000	3.5	1.92	0.206 (8.1)

(a) All laminates were 10.2 x 10.2 cm (4 x 4 inches).

(b) Unless otherwise noted, laminates were imidized as shown, inserted in 232°C (450°F) preheated die, held 10 minutes at contact pressure, subjected to pressure shown and brought to 316°C (600°F) in 20 minutes and held one hour.

(c) This laminate was installed unimidized in a cold die and press and brought to 316°C (600°F) at 5.6°C/minute (10°F/min.) and held one hour at 316°C (600°F). Pressure was applied at 254°C (490°F).

(d) Laminate was imidized as shown, inserted in a preheated die at 316°C (600°F), held 60 seconds, and pressure applied.

TABLE V

RESULTS OF 316^{o}C (600^{o}F) FLEXURE TESTS ON NON-POSTCURED DIE MOLDED LAMINATES

Reinforcement	Laminate No.	Imidization Time/Temp. hr/^{o}C (^{o}F)	Mold Pressure MPa	Mold Pressure Psi	Flexure Strength MPa	Flexure Strength Ksi	Flexure Modulus GPa	Flexure Modulus Msi
T-300 (S)	772-6	1/204 (400)	1.4	200	432	62.7	40	5.8
T-300 (S)	772-7	2/204 (400)	6.9	1000	381	55.2	37	5.4
T-300 (HC)	772-11	1/204 (400)	6.9	1000	426	61.8	47	6.8
T-300 (HC)	772-12	1/204 (400)	1.4	200	117	17.0	-	-
T-300 (HC)	772-15	1/204 (400)	1.4	200	450	65.3	41	6.0
S-6581	722-20	1/204 (400)	1.4	200	437	63.4	23	3.4

NOTE: Values shown represent average of three determinations.

TABLE VI

316°C (600°F) FLEXURAL AND SHEAR DATA ON THREE PMR II/S-6581 AUTOCLAVED PANELS USING NR-050X LOT -87

	Flexure Strength[a]		Flexure Modulus[a]		Short Beam Shear Strength[b]	
	MPa	Ksi	GPa	Msi	MPa	Ksi
Panel 772-84/1[c]	419	60.8	26	3.7	31	4.5
Panel 772-84/4[c]	518	75.2	26	3.8	32	4.6
Panel 772-84/5[d]	456	66.1	25	3.6	32	4.6

(a) Average of four determinations.
(b) Average of six determinations.
(c) Autoclaved with unimidized material and a caul plate.
(d) Autoclaved with unimidized material and bleeder cloth on surface.

(-) All 102 x 102 x 2.4 mm panels autoclaved and postcured together.
(-) NR-050X sample lot -87 obtained in October 1976.

TABLE VII

MECHANICAL TEST DATA ON DIE MOLDED PMR II/S-6581 LAMINATE

	Flexure Strength		Flexure Modulus		Short Beam Shear	
	MPa	Ksi	GPa	Msi	MPa	Ksi
Room Temp.	687	99.6	32	4.6	80	11.6
	687	99.6	↓	↓	81	11.7
	702	101.8	↓	↓	83	12.0
Avg.	692	100.3	32	4.6	81	11.8
316°C (600°F)	541	78.4	30	4.3	45	6.5
	540	78.3	↓	↓	35	5.1
	531	77.0	↓	↓	41	5.9
Avg.	537	77.9	30	4.3	40	5.8

(-) Laminate number 826-24
(-) Estimated fiber volume: 53.6 v/o
(-) Laminate postcured 16 hours @ 316°C (600°F)
(-) Molding pressure 3.4 MPa (500 psi)

TABLE VIII

PMR-15 DIE MOLDED LAMINATE DATA

Reinforcement	Laminate No.	Fiber Volume v/o	Thickness mm (mils)	Specific Gravity		Weight Loss in Postcure[a] w/o
				As-Molded	Postcured	
S-6581	772-30	51.0	2.3 (90)	1.90	-	1.2
↓	772-31	-	2.4 (94)	1.89	-	1.3
↓	772-32	-	2.3 (92)	1.91	-	1.4
A-S	772-49	-	2.3 (91)	1.55	-	1.5
↓	772-50	52.1	↓	↓	1.56	1.6
↓	772-51	-	↓	↓	-	1.7

NOTE: (a) Postcured at 343°C (650°F) for 16 hours.

TABLE IX

SHORT BEAM SHEAR STRENGTH RESULTS ON DIE MOLDED S-6581/PMR-15

	Room Temperature		316°C (600°F)	
	MPa	Ksi	MPa	Ksi
Panel 772-30 As-Molded (a)	74.5	10.8	27.6	4.0
	80.7	11.7	29.0	4.2
	75.8	11.0	30.3	4.4
Avg.	77.2	11.2	29.0	4.2
Panel 772-30 Postcured (b)	47.6	6.9	35.2	5.1
	47.6	6.9	35.2	5.1
	47.6	6.9	35.9	5.2
Avg.	47.6	6.9	35.2	5.1

NOTES: (a) 33.5 w/o resin (avg. of 3 results)

(b) 33.2 w/o resin (avg. of 3 results)

TABLE X

FLEXURE TEST RESULTS ON DIE MOLDED S-6581/PMR-15

	Room Temperature				316°C (600°F)			
	Strength		Modulus		Strength		Modulus	
	MPa	Ksi	GPa	Msi	MPa	Ksi	GPa	Msi
Panel 772-30 As-Molded (a)	713	103.4	32	4.7	410	59.5	24	3.5
	763	110.7	30	4.4	357	51.8	25	3.6
	773	112.2	32	4.6	412	59.7	26	3.7
Avg.	750	108.8	32	4.6	393	57.0	25	3.6
Panel 772-30 Postcured (b)	523	75.8	27	3.9	446	64.7	26	3.8
	537	77.9	27	3.9	414	60.1	26	3.7
	570	82.7	28	4.0	460	66.7	26	3.7
Avg.	543	78.8	27	3.9	440	63.8	26	3.7

NOTES: (a) 33.5 w/o resin (avg. of 3 results)
(b) 33.2 w/o resin (avg. of 3 results)

TABLE XI

SHORT BEAM SHEAR STRENGTH RESULTS ON DIE MOLDED A-S/PMR-15

		Room Temperature		316°C (600°F)	
		MPa	Ksi	MPa	Ksi
Panel 772-50 As-Molded		113	16.4	40	5.8
		112	16.2	39	5.7
		112	16.2	37	5.3
	Avg.	112	16.3	39	5.6
Panel 772-50 Postcured		106	15.4	57	8.3
		110	16.0	53	7.7
		99	14.4	54	7.8
	Avg.	105	15.3	54	7.9

TABLE XII

FLEXURE TEST RESULTS ON DIE MOLDED A-S/PMR-15

	Room Temperature				316°C (600°F)			
	Strength		Modulus		Strength		Modulus	
	MPa	Ksi	GPa	Msi	MPa	Ksi	GPa	Msi
Panel 772-50 As-Molded	1575	228.4	97.2	14.1	749	108.6	90.3	13.1
	1524	221.0	97.9	14.2	1004	145.6	89.6	13.0
	1538	223.0	95.8	13.9	856	124.1	91.0	13.2
Avg.	1545	224.1	97.2	14.1	869	126.1	90.3	13.1
Panel 772-50 Postcured	1155	167.5	95.8	13.9	1018	147.7	89.6	13.0
	1229	178.3	99.3	14.4	1083	157.1	93.8	13.6
	1362	197.5	95.8	13.9	1122	162.7	94.5	13.7
Avg.	1249	181.1	97.2	14.1	1074	155.8	92.4	13.4

TABLE XIII

20 x 20 CM AUTOCLAVE MOLDED PMR-15 LAMINATE DATA

Reinforcement	Laminate No.	Fiber Volume v/o	Thickness mm (mils)	Specific Gravity		Weight Loss in Postcure(a) w/o
				As-Molded	Postcured	
S-6581	772-35	-	2.6(102)	1.89	1.87	1.4
↓	772-36	50.3	↓	1.88	1.87	1.3
	772-37A			1.88	-	1.3
	772-37AA			1.88		1.5
T-300 (sized)	772-38A	51.2	2.0(80)	1.52	1.53	1.5
↓	772-39A	-	↓	-	-	1.6
	772-48/1	-		1.53	-	1.2
T-300 (Heat cleaned)	772-38AA	52.4	2.0(80)	1.52	1.53	1.6
↓	772-39AA	-	↓	1.52	-	1.6
	772-48/2	-		1.52	-	1.3

(a) Post cure at 343^{o}C (650^{o}F) for 16 hours.

TABLE XIV

SHORT BEAM SHEAR STRENGTH RESULTS ON AUTOCLAVE MOLDED S-6581/PMR-15

		Room Temperature		316°C (600°F)	
		MPa	Ksi	MPa	Ksi
Panel 772-36 As-Molded(a)		75.2	10.9	14	2.1
		76.5	11.1	21	3.0
		75.8	11.0	12	1.7
	Avg.	75.8	11.0	16	2.3
Panel 772-36 Postcured		38	5.5	34	5.0
		37	5.3	34	5.0
		34	5.0	35	5.1
	Avg.	37	5.3	34	5.0
Panel 772-35 Postcured(b)		33	4.8	37	5.4
		37	5.3	32	4.6
		34	4.9	32	4.7
	Avg.	34	5.0	34	4.9

(a) Molded with caul plate.
(b) Molded without caul plate.

TABLE XV

FLEXURE TEST RESULTS ON AUTOCLAVE MOLDED S-6581/PMR-15

	Room Temperature				316°C (600°F)			
	Strength		Modulus		Strength		Modulus	
	MPa	Ksi	GPa	Msi	MPa	Ksi	GPa	Msi
Panel 772-36[a]	714	103.5	28	4.0	264	38.3	16	2.3
As-Molded	642	93.2	↓	4.0	367	53.3	21	3.1
↓	656	95.1	↓	4.0	374	54.2	22	3.2
↓ Avg.	671	97.3	↓	4.0	335	48.6	20	2.9
Panel 772-36	678	98.3	26	3.7	381	55.3	23	3.4
Postcured	463	67.1	↓	3.7	516	74.8	25	3.6
↓	667	96.7	↓	3.7	444	64.3	23	3.3
↓ Avg.	603	87.4	↓	3.7	447	64.8	23	3.4
Panel 772-35[b]	403	58.5	22	3.2	356	51.7	21	3.0
Postcured	437	63.4	23	3.4	341	49.4	↓	3.0
↓	376	54.5	20	2.9	383	55.6	↓	3.0
↓ Avg.	403	58.8	22	3.2	360	52.2	↓	3.0

(a) Molded with caul plate.
(b) Molded without caul plate.

TABLE XVI

SHORT BEAM SHEAR STRENGTH RESULTS ON AUTOCLAVE MOLDED T-300/PMR-15

		Room Temperature		316^oC (600^oF)	
		MPa	Ksi	MPa	Ksi
Panel 772-38A As-Molded(a)		61	8.8	32	4.7
		57	8.2	36	5.2
		61	8.8	30	4.3
	Avg.	59	8.6	32	4.7
Panel 772-38A Postcured(a)		46	6.6	43	6.2
		46	6.7	42	6.1
		48	6.9	41	6.0
	Avg.	46	6.7	42	6.1
Panel 772-38AA As-Molded(b)		57	8.2	33	4.8
		53	7.3	32	4.7
		50	7.2	38	5.5
	Avg.	52	7.6	34	5.0
Panel 772-38AA Postcured(b)		47	6.8	34	5.0
		45	6.5	35	5.1
		44	6.4	38	5.5
	Avg.	46	6.6	36	5.2

(a) Sized Cloth.
(b) Cloth heat cleaned prior to resin application.

TABLE XVII

FLEXURE TEST RESULTS ON AUTOCLAVE MOLDED T-300/PMR-15

	Room Temperature				316°C (600°F)			
	Strength		Modulus		Strength		Modulus	
	MPa	Ksi	GPa	Msi	MPa	Ksi	GPa	Msi
Panel 772-38A	749.5	108.7	55	8.0	343	49.8	34	5.0
As-Molded(a)	745.3	108.1	54	7.9	385	55.8	42	6.1
	795.0	115.3	56	8.1	561	81.4	51	7.4
Avg.	763.2	110.7	55	8.0	430	62.3	43	6.2
Panel 772-38A	746	108.2	51	7.4	543	78.7	52	7.6
Postcured(a)	596	86.5	53	7.7	609	88.3	52	7.6
	593	86.0	56	8.1	632	91.6	54	7.8
Avg.	645	93.6	53	7.7	594	86.2	53	7.7
Panel 772-38AA	671	97.3	55	8.0	500	72.5	46	6.7
As-Molded(b)	656	95.2	53	7.7	557	80.8	50	7.2
	713	103.4	54	7.9	521	75.5	53	7.7
Avg.	680	98.6	54	7.9	526	76.3	50	7.2
Panel 772-38AA	575	83.4	54	7.9	518	75.2	54	7.8
Postcured(b)	669	97.0	52	7.5	488	70.8	52	7.6
	762	110.5	54	7.8	569	82.5	52	7.5
Avg.	669	97.0	53	7.7	525	76.2	52	7.6

(a) Sized cloth.
(b) Heat cleaned cloth.

TABLE XVIII

$316^{o}C$ ($600^{o}F$) FLEXURAL AND SHEAR DATA ON PMR II/S-6581[(a)]

		Flex. Strength		Flex. Modulus		Short Beam Shear Strength	
		MPa	Ksi	GPa	Msi	MPa	Ksi
Panel 772-90		504	73.1	25	3.6	39	5.7
As-Molded		496	71.9	26	3.8	37	5.3
		490	71.1	26	3.7	37	5.4
	Avg.	496	72.0	26	3.7	38	5.5
Panel 772-90		454	65.9	25	3.6	34	4.9
Postcured $343^{o}C$		465	67.5	24	3.5	34	5.0
($650^{o}F$)		456	66.1	26	3.7	35	5.1
	Avg.	459	66.5	25	3.6	34	5.0

(a) Autoclaved Panel using NR-050X Lot -30.

TABLE XIX

316°C (600°F) FLEXURAL AND SHEAR DATA ON PMR II/WOVEN T-300 AUTOCLAVED PANELS USING NR-050X LOT -30

	Flex. Strength		Flex. Modulus		Short Beam Shear Strength	
	MPa	Ksi	GPa	Msi	MPa	Ksi
Panel 772-98	596	86.5	53	7.7	40	5.8
As-Molded	558	80.9	54	7.8	42	6.1
	554	80.3	52	7.6	39	5.7
Avg.	570	82.6	53	7.7	41	5.9
Panel 772-98	568	82.4	52	7.5	43	6.3
Postcured 343°C	554	80.3	52	7.5	43	6.2
(650°F)	603	87.5	54	7.8	39	5.7
Avg.	575	83.4	52	7.6	42	6.1

TABLE XX

260^{o}C (500^{o}F) ISOTHERMAL WEIGHT LOSSES

Material	Laminate No.	Hours	% Weight Loss
T-300 PMR-15 Auto. Molded	772-95T	312	1.5
		591	2.3
		1015	2.0
A-S PMR-15 Die Molded	826-1	312	1.1
		591	1.2
		1015	1.5
S-6581 PMR-15 Auto. Molded	772-95S	312	1.0
		591	1.1
		999	1.4
		2000	2.6

TABLE XXI

$260^{o}C$ ($500^{o}F$) ISOTHERMAL MECHANICAL TEST DATA ON AUTOCLAVE MOLDED WOVEN T-300/PMR-15 COMPOSITE

Exposure Time hrs	Exposure & Test Temperature ^{o}C (^{o}F)	Flexure Strength MPa	Flexure Strength Ksi	Flexure Strength % Retention	Flexure Modulus GPa	Flexure Modulus Msi	Short Beam Shear Strength MPa	Short Beam Shear Strength Ksi	Short Beam Shear Strength % Retention
	RT	684	99.2	-	55.1	8.0	60	8.7	-
0.5	260 (500)	689	100.0	100	53.8	7.8	46	6.6	100
312	↓	675	97.9	98	53.1	7.7	46	6.6	100
591		639	92.7	93	52.4	7.6	46	6.6	100
1015		592	85.8	86	49.6	7.2	43	6.3	95

(-) Laminate number 772-95T

(-) Laminate postcured 16 hours at $316^{o}C$ ($600^{o}F$)

(-) All values represent average of three specimens

(-) Fiber volume determined to be 51.9 v/o (original)

TABLE XXII

260°C (500°F) ISOTHERMAL MECHANICAL TEST DATA ON DIE MOLDED UNIDIRECTIONAL A-S/PMR-15 COMPOSITE

Exposure Time hrs	Exposure & Test Temperature °C (°F)	Flexure Strength			Flexure Modulus		Short Beam Shear Strength		
		MPa	Ksi	% Retention	GPa	Msi	MPa	Ksi	% Retention
-	RT	1302	188.8	-	97.2	14.1	103	15.0	-
0.5	260 (500)	1230	178.4	100	96.5	14.0	59	8.6	100
312	↓	1247	180.9	100	91.7	13.3	54	7.8	91
591		1243	180.3	100	96.5	14.0	55	8.0	93
1015		1152	167.1	94	95.8	13.9	57	8.3	97

(-) Laminate number 826-1
(-) Laminate postcured 16 hours at 316°C (600°F)
(-) All values represent average of three specimens
(-) Fiber volume determined to be 52.6 v/o (original)

TABLE XXIII

$260^{o}C$ ($500^{o}F$) ISOTHERMAL MECHANICAL TEST DATA ON AUTOCLAVE MOLDED WOVEN S-6581 GLASS/PMR-15 COMPOSITES

Exposure Time hrs	Exposure & Test Temperature ^{o}C (^{o}F)	Flexure Strength MPa	Flexure Strength Ksi	Flexure Strength % Retention	Flexure Modulus GPa	Flexure Modulus Msi	Short Beam Shear Strength MPa	Short Beam Shear Strength Ksi	Short Beam Shear Strength % Retention
-	RT	605	87.8	-	27	3.9	52	7.5	-
0.5	260 (500)	458	66.4	100	25	3.6	34	5.0	100
312	↓	460	66.7	100	26	3.7	39	5.7	↓
591		389	56.4	85	25	3.6	41	5.9	
999		385	55.9	84	25	3.6	38	5.5	
2000		371	53.8	81	26	3.7	38	5.5	

(-) Laminate number 772-95S
(-) Laminate postcured 16 hours at $316^{o}C$ ($600^{o}F$)
(-) All values represent average of three specimens
(-) Fiber volume determined to be 50.7 v/o (original)

TABLE XXIV

316°C (600°F) ISOTHERMAL WEIGHT LOSSES

Material	Laminate No.	Hours	% Weight Loss
S-6581 PMR-15 Auto. Molded	772-96S	294	2.7
		600	8.2
		1008	16.6
		1416	22.8
		2000	29.9
S-6581 PMR-15 Die Molded	826-2	294	4.0
		600	9.3
		1008	18.8
		2000	31.7
S-6581 PMR II Auto. Molded	826-27 826-25	336	2.4
		598	5.2
		1006	8.6
		2014	11.8
HM-S(a) PMR-15 Die Molded	767-59	294	1.6
		600	3.0
		1008	6.1
		1416	9.4
		2000	15.8

NOTE: (a) Control panel

TABLE XXV

$316^{o}C$ ($600^{o}F$) ISOTHERMAL MECHANICAL TEST DATA ON AUTOCLAVE MOLDED WOVEN S-6581/PMR-15 COMPOSITES

Exposure Time hrs	Exposure & Test Temperature ^{o}C (^{o}F)	Flexure Strength MPa	Ksi	% Retention	Flexure Modulus GPa	Msi	Short Beam Shear Strength MPa	Ksi	% Retention
-	RT	610	88.5	-	28	4.1	68	9.9	-
0.5	316 (600)	499	72.4	100	26	3.8	33	4.8	100
294	↓	344	49.9	69	22	3.2	35	5.1	100
600	↓	99	14.3	20	12	1.7	25	3.6	75
1000	↓	Too badly degraded to test.							

(-) Laminate number 772-96S
(-) Laminate postcured 16 hours at $316^{o}C$ ($600^{o}F$)
(-) All values represent average of three specimens
(-) Fiber volume determined to be 51.1 v/o (original)

TABLE XXVI

316^oC (600^oF) ISOTHERMAL MECHANICAL TEST DATA ON DIE MOLDED WOVEN S-6581 GLASS/PMR-15 COMPOSITE

Exposure Time hrs	Exposure & Test Temperature ^oC (^oF)	Flexure Strength MPa	Flexure Strength Ksi	Flexure Strength % Retention	Flexure Modulus GPa	Flexure Modulus Msi	Short Beam Shear Strength MPa	Short Beam Shear Strength Ksi	Short Beam Shear Strength % Retention
-	RT	654	94.9	-	30	4.3	54	7.8	-
0.5	316 (600)	489	70.9	100	26	3.8	31	4.5	100
294	↓	288	41.8	59	21	3.1	28	4.1	91
600	↓	112	16.2	23	12	1.8	21	3.1	69
1000	↓	Too badly degraded to test.							

(-) Laminate number 826-2
(-) Laminate postcured 16 hours at 316^oC (600^oF)
(-) All values represent average of three specimens
(-) Fiber volume determined to be 47.9 v/o (original)

TABLE XXVII

316^oC (600^oF) ISOTHERMAL MECHANICAL TEST DATA ON AUTOCLAVE MOLDED WOVEN S-6581/PMR II COMPOSITES

Laminate No.	Exposure Time hrs	Exposure & Test Temperature ^oC	^oF	Flexure Strength MPa	Ksi	% Retention	Flexure Modulus GPa	Msi	Short Beam Shear Strength MPa	Ksi	% Retention
826-25	-	RT	RT	-	-	-	-	-	80	11.6	-
826-27	-	RT	RT	-	-	-	-	-	81	11.8	-
826-25	0.5	316	600	523	75.8	100	28	4.0	37	5.3	100
826-27	0.5	↓	↓	491	71.2	100	28	4.0	32	4.7	100
826-27	336	↓	↓	259	37.6	53	25	3.6	30	4.3	91
826-25	598	↓	↓	164	23.8	31	22	3.2	18	2.6	49
826-27	1006	↓	↓	141	20.5	29	22	3.2	10	1.4	30
826-25	2014	↓	↓	100	14.5	19	14	2.1	7	1.0	19
826-27	2014	↓	↓	92	13.3	19	14	2.1	7	1.0	21

(-) Laminate numbers 826-25 & 826-27
(-) Laminate postcured 16 hours at 316^oC (600^oF)
(-) All values represent average of three specimens
(-) Fiber volumes determined to be 54.7 & 52.4 v/o (original)

TABLE XXVIII

FOUR-POINT FLEXURE STRENGTH RESULTS ON THICK PMR-15 LAMINATES

Laminate Identity	Gage Length Configuration	Span/Depth Ratio	Strength MPa	Strength Ksi
T-300/Autoclave Molded	Straight	30	659	95.6
Lam. No. 826-16	Straight	30	699	101.4
T-300/Die Molded	Reduced	46	792	114.9
	Reduced	46	751	108.9
S-6581/Autoclave Molded	Straight	23	567	82.3
Lam. No. 826-17	Reduced	↓	541	78.5
	Reduced	↓	553	80.2
S-6581/Die Molded Lam. No. 826-13	Reduced	25	637	92.4
A-S/Die Molded	Straight	42	1199	173.9
Lam. No. 826-15	Straight	41	1283	186.1
	Reduced	43	1134	164.5

(-) Thickness range of laminates from 3.7 to 7.3 mm (0.146-0.289 inches).

(-) Inner span 5.7 cm (2.25 inches), outer span 17.1 cm (6.75 inches).

TABLE XXIX

FOUR-POINT FLEXURE STRENGTH RESULTS ON THIN PMR-15 LAMINATES

Laminate Identity	Gage Length Configuration	Span/Depth Ratio	Strength	
			MPa	Ksi
T-300/Autoclave Molded	Straight	35	705	102.2
Lam. No. 772-94	Straight	35	682	98.9
	Reduced	49	616	89.3
	↓	↓	585	84.9
			581	84.3
S-6581/Die Molded	Straight	29	631	91.5
Lam. No. 826-4	↓	↓	590	85.5
			586	85.0
	Reduced	29	668	96.9
	↓	↓	661	95.9
			682	98.9
A-S/Die Molded	Straight	41	1270	184.2
Lam. No. 772-100	↓	↓	1105	160.3
			1094	158.6
	Reduced	41	1201	174.2
	↓	↓	1108	160.7
			1179	171.0

(-) Thickness range of laminates from 0.20 to 0.24 mm (0.077-0.093 inches).

TABLE XXX

PMR-15 COMPOSITE STRESS LEVELS AT 1 x 10^7 FLEXURAL FATIGUE CYCLES

	T-300 Autoclaved	S-6581 Autoclaved	S-6581 Die Molded
Range			
MPa	191-253	65-84	74-91
Ksi	27.7-36.7	9.4-12.2	10.8-13.2
% of Ultimate[(a)]	29-38	11-14	13-16
Average			
MPa	222	74	83
Ksi	32.2	10.8	12.0
% of Ultimate[(a)]	33	13	14

Note: (a) % of ultimate static flexural strength

TABLE XXXI

RETAINED FOUR-POINT FLEXURE STRENGTH RESULTS FROM NON-FAILED FATIGUE SPECIMENS

	Fatigue Exposure				Post-Fatigue Flexural Results			
Material Identification	Fatigue Stress MPa	Ksi	% of Ultimate Stress Applied	Fatigue Cycles Accumulated (Millions)	Span/Depth Ratio	Strength MPa	Ksi	% of Ultimate Strength Retained
T-300/Autoclaved(a)	165	23.9	25	2.3	45	694	100.6	100
Lam. No. 826-10	197	28.5	29	7.8	45	685	99.3	100
S-6581/Autoclaved(b)	79	11.4	18	15.3	24	542	78.6	93
Lam. No. 826-18								
S-6581/Die(b)	79	11.4	14	7.1	25	598	86.8	100
Lam. No. 826-13								
S-6581/Die(b)	85	12.4	15	2.6	25	616	89.4	100
Lam. No. 826-8	108	15.7	19	2.4	25	426	61.8	73

NOTES: (a) Control static flexure failure stress value equal to 669 MPa (97.0 Ksi).

(b) Control static flexure failure stress value equal to 581 MPa (84.3 Ksi).

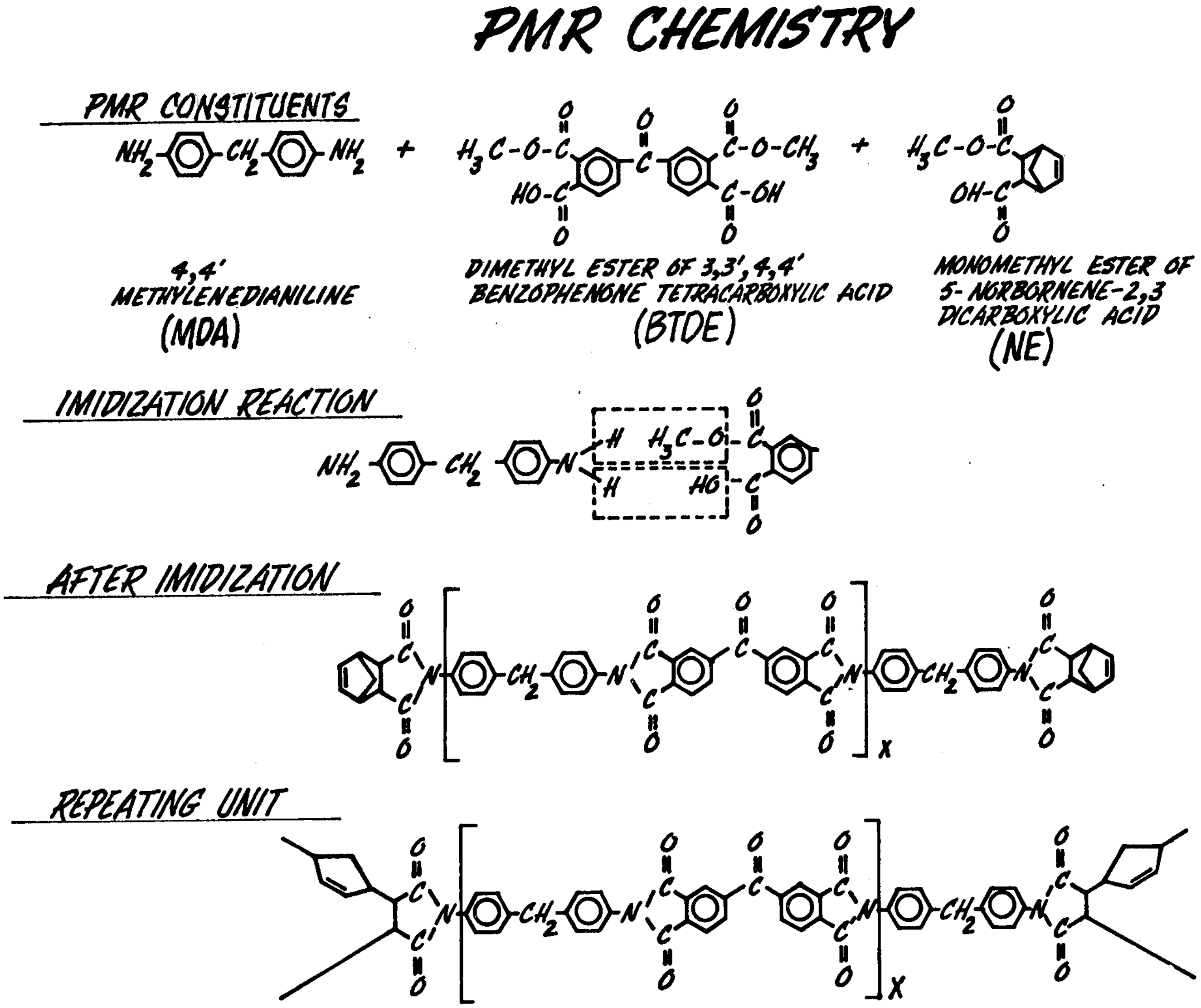


Figure 1. PMR Polyimide Chemistry.

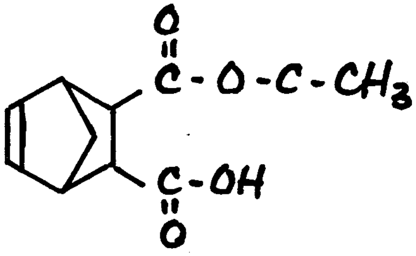
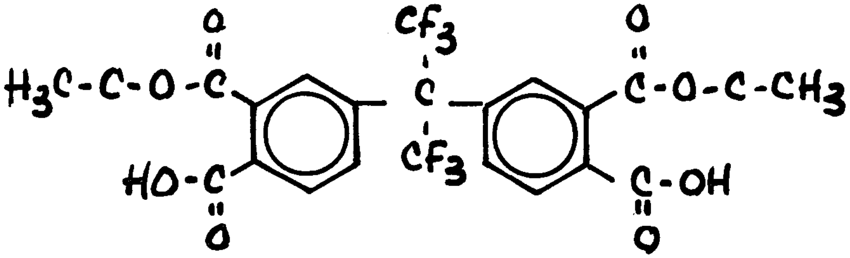
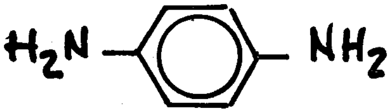
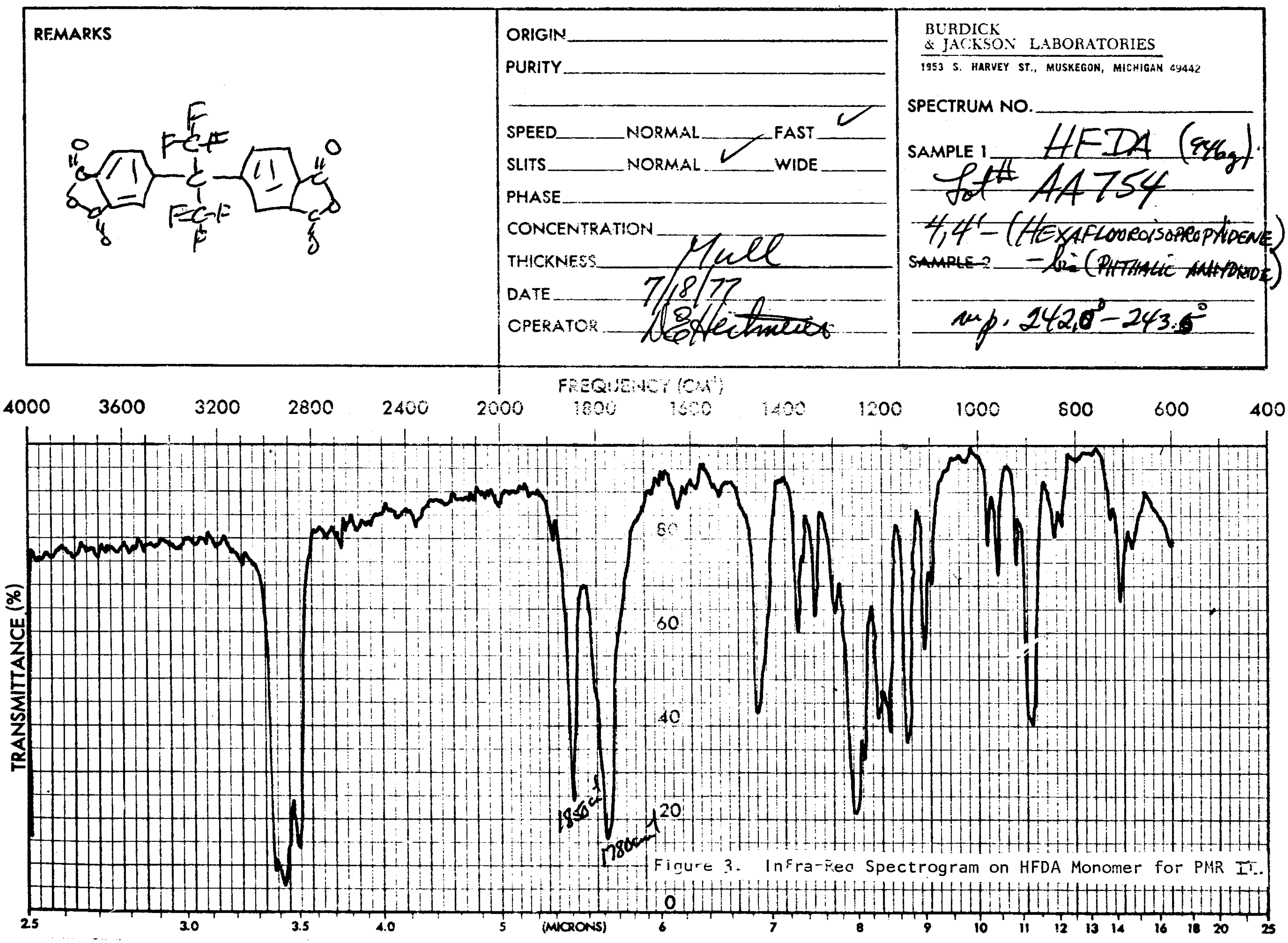
STRUCTURE	NAME	ABBREVIATION
	MONOETHYL ESTER OF 5-NORBORNENE-2, 3-DICARBOXYLIC ACID	NE
	DIETHYLESTER OF 4, 4'-(HEXAFLUOROISOPROPYLIDENE)-BIS (PHTHALIC ACID)	HFDE
	PARA-PHENYLENEDIAMINE	PPDA

Figure 2. Monomers Used in the Preparation of Second Generation PMR Polyimides.



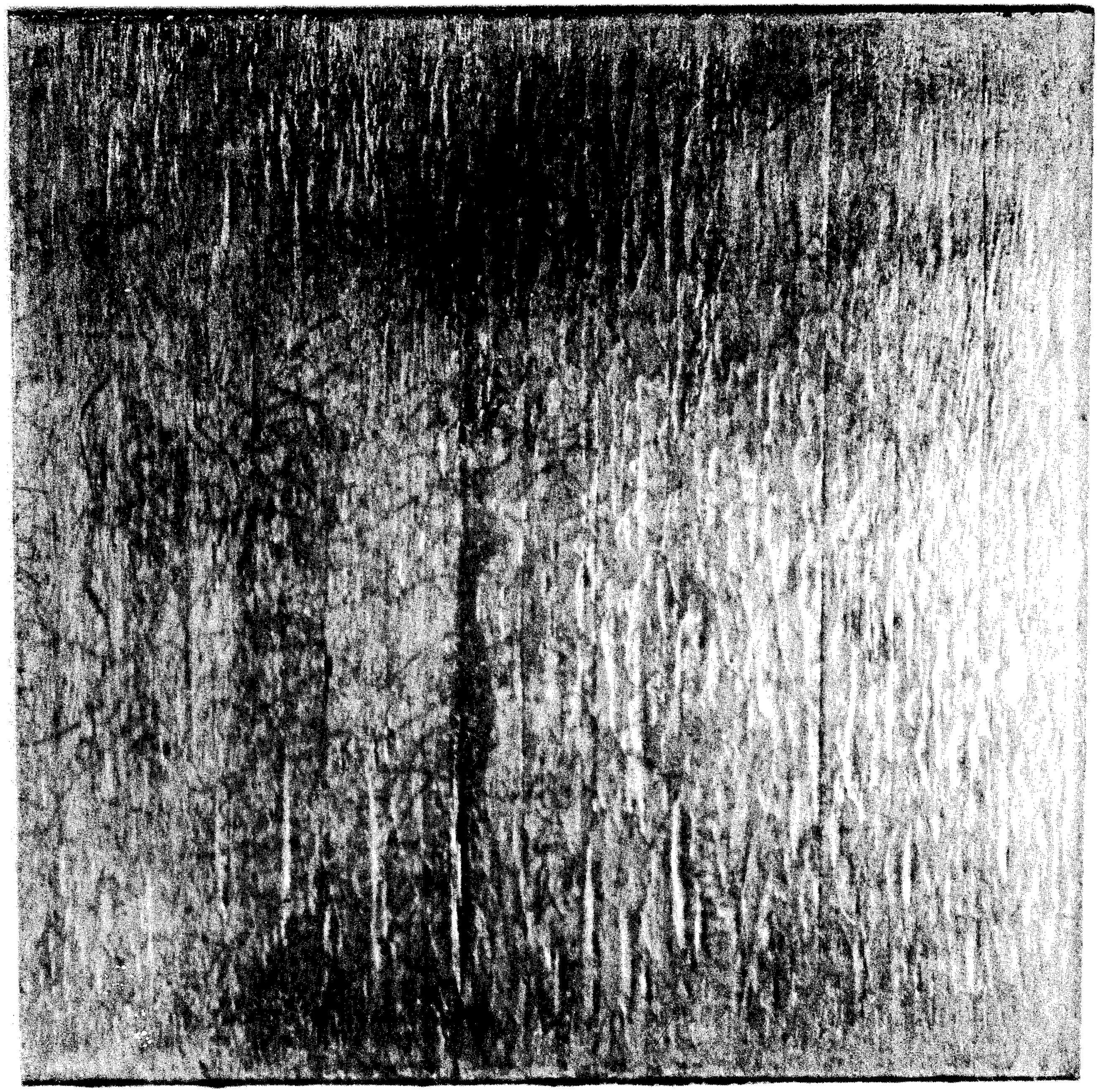
REMARKS

ORIGIN
PURITY
SPEED NORMAL FAST ✓
SLITS NORMAL ✓ WIDE
PHASE
CONCENTRATION
THICKNESS Mull
DATE 7/8/77
OPERATOR Heitmeier

BURDICK
& JACKSON LABORATORIES
1953 S. HARVEY ST., MUSKEGON, MICHIGAN 49442

SPECTRUM NO.
SAMPLE 1 HFDA (99%g).
Lot# AA754
4,4'-(HEXAFLOUROISOPROPYLIDENE)
~~SAMPLE 2~~ -bis (PHTHALIC ~~ANHYDRIDE~~)
mp. 242.0°-243.5°

Figure 3. Infra-Red Spectrogram on HFDA Monomer for PMR II.



Mag. 1.7X

Figure 4. Laminate Showing Surface Defects Encountered with the First Lot of A-S/PMR-15.

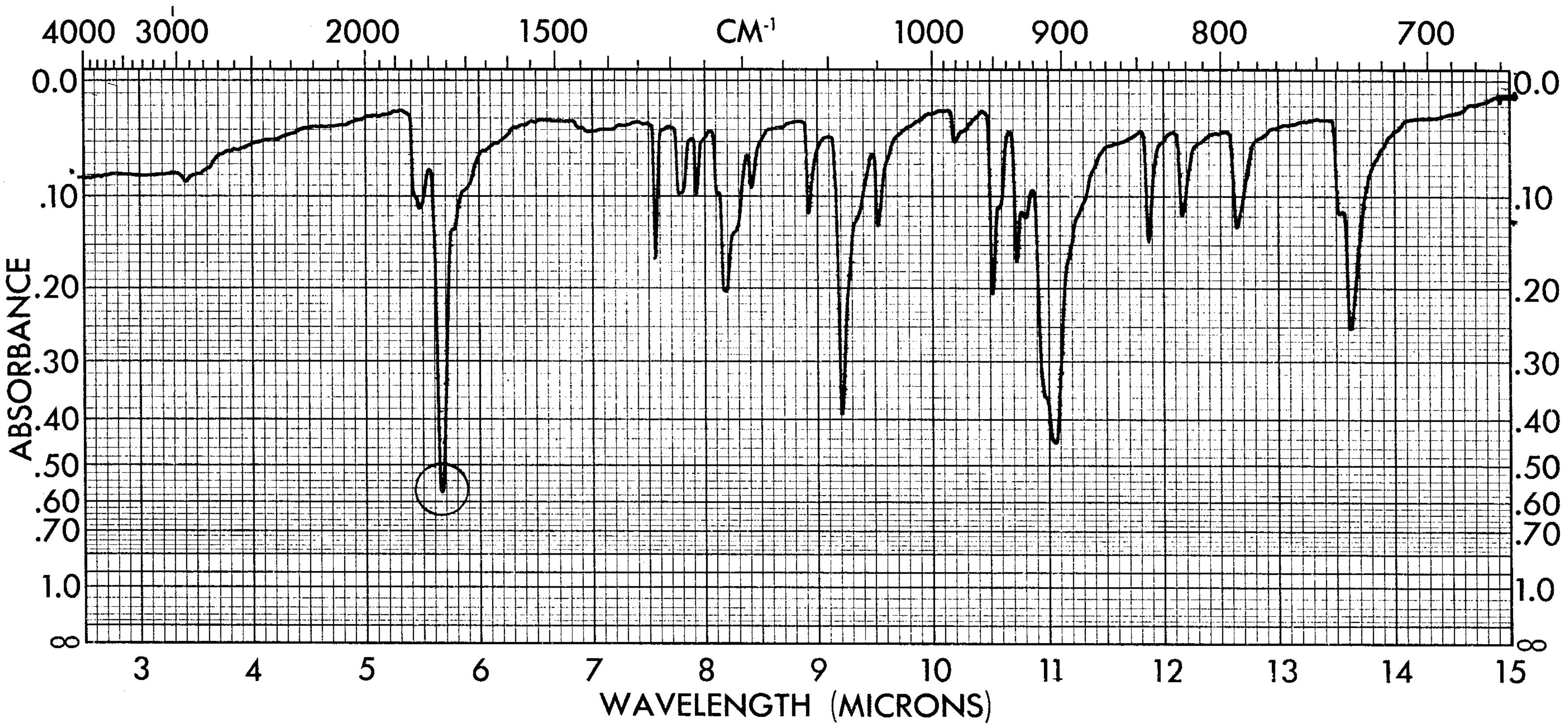


Figure 5. Infra-Red Spectrogram of Pure Norbornene Anhydride.

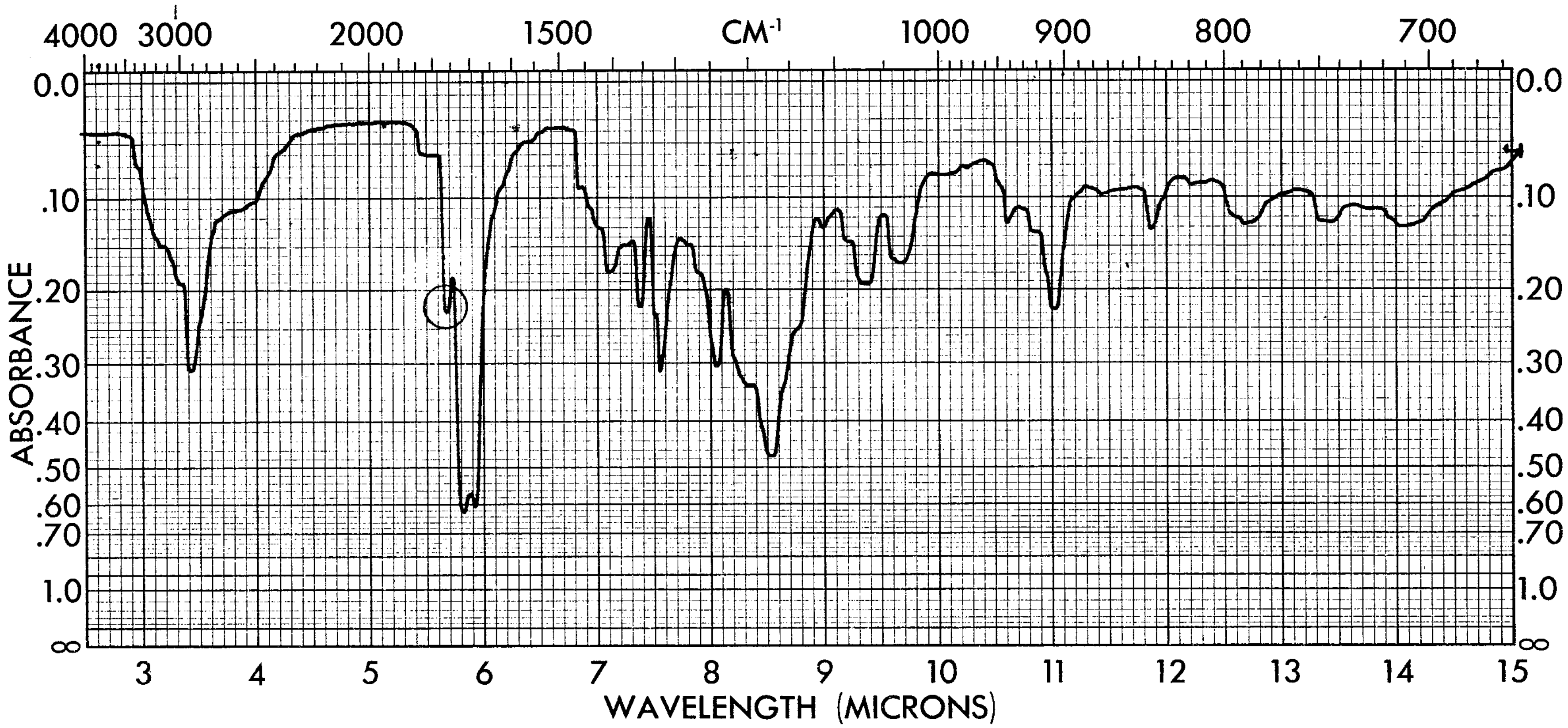


Figure 6. Infra-Red Spectrogram of Ester-Acid Solution with Anhydride Deliberately Added.

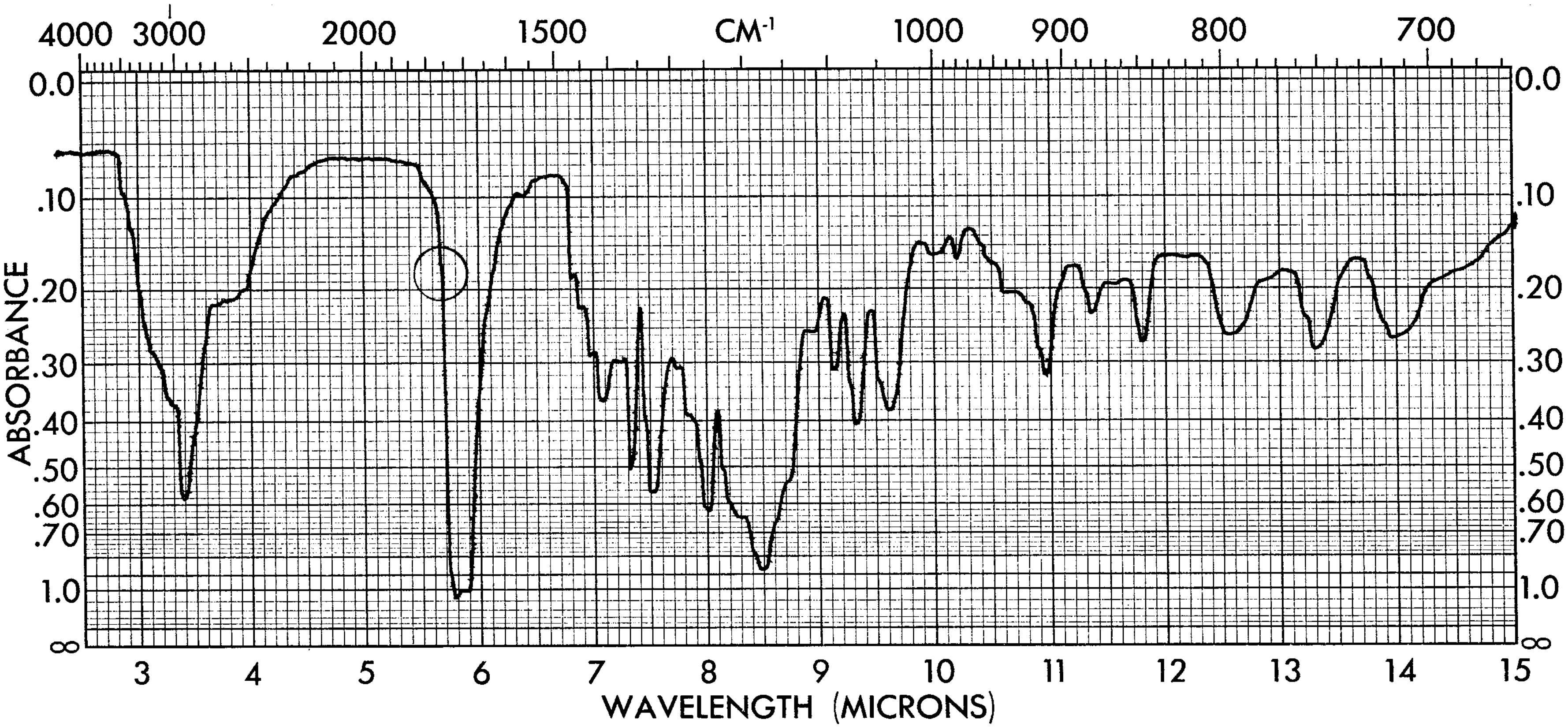


Figure 7. Infra-Red Spectrogram of the Ester-Acid Solution Ready for Blending.

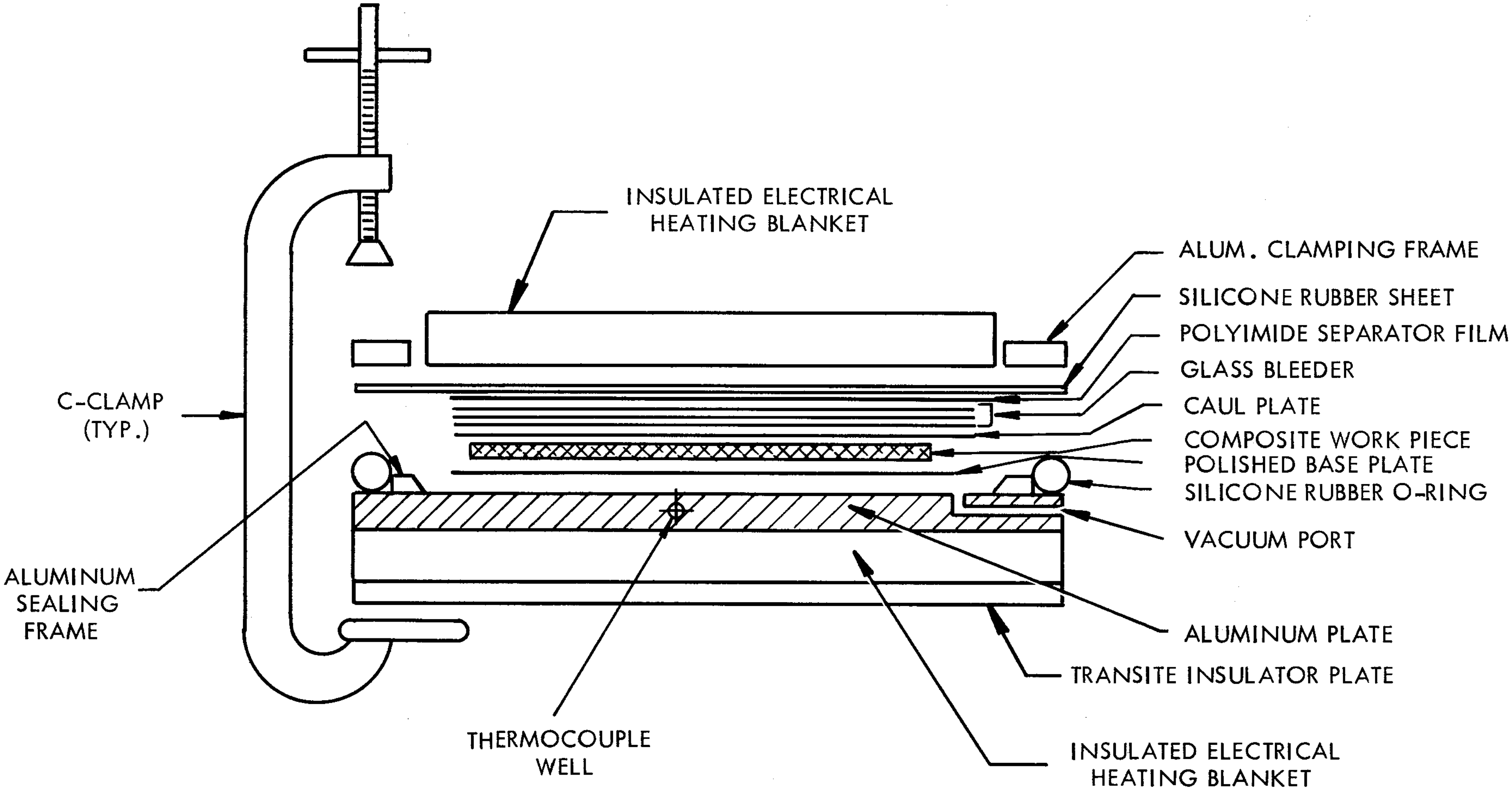


Figure 8. Autoclave Bag and Blanket-Heated Tool Concept.

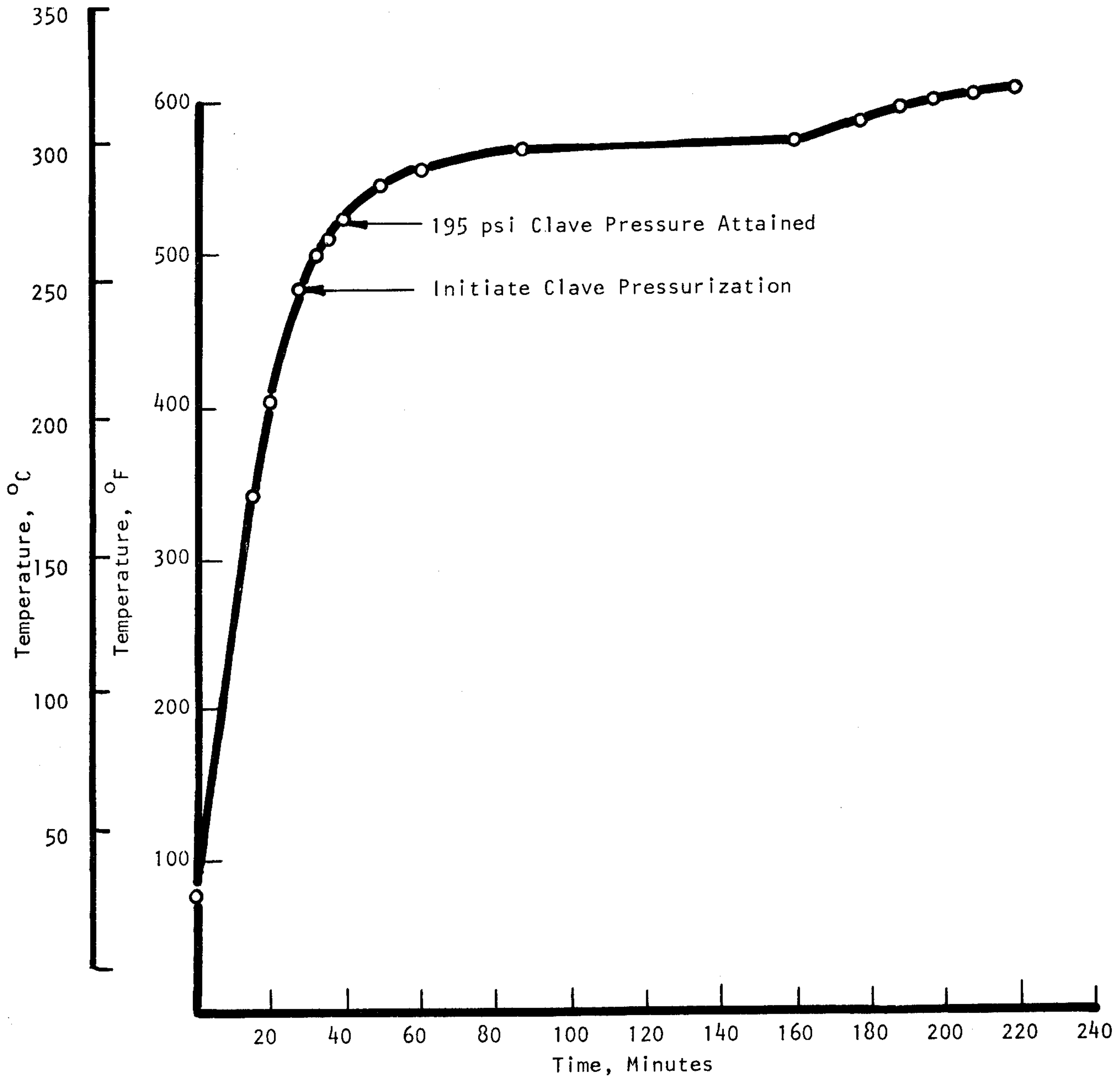


Figure 9. Temperature Rise of Steel Tool in First Autoclave Run with Heating Blankets.

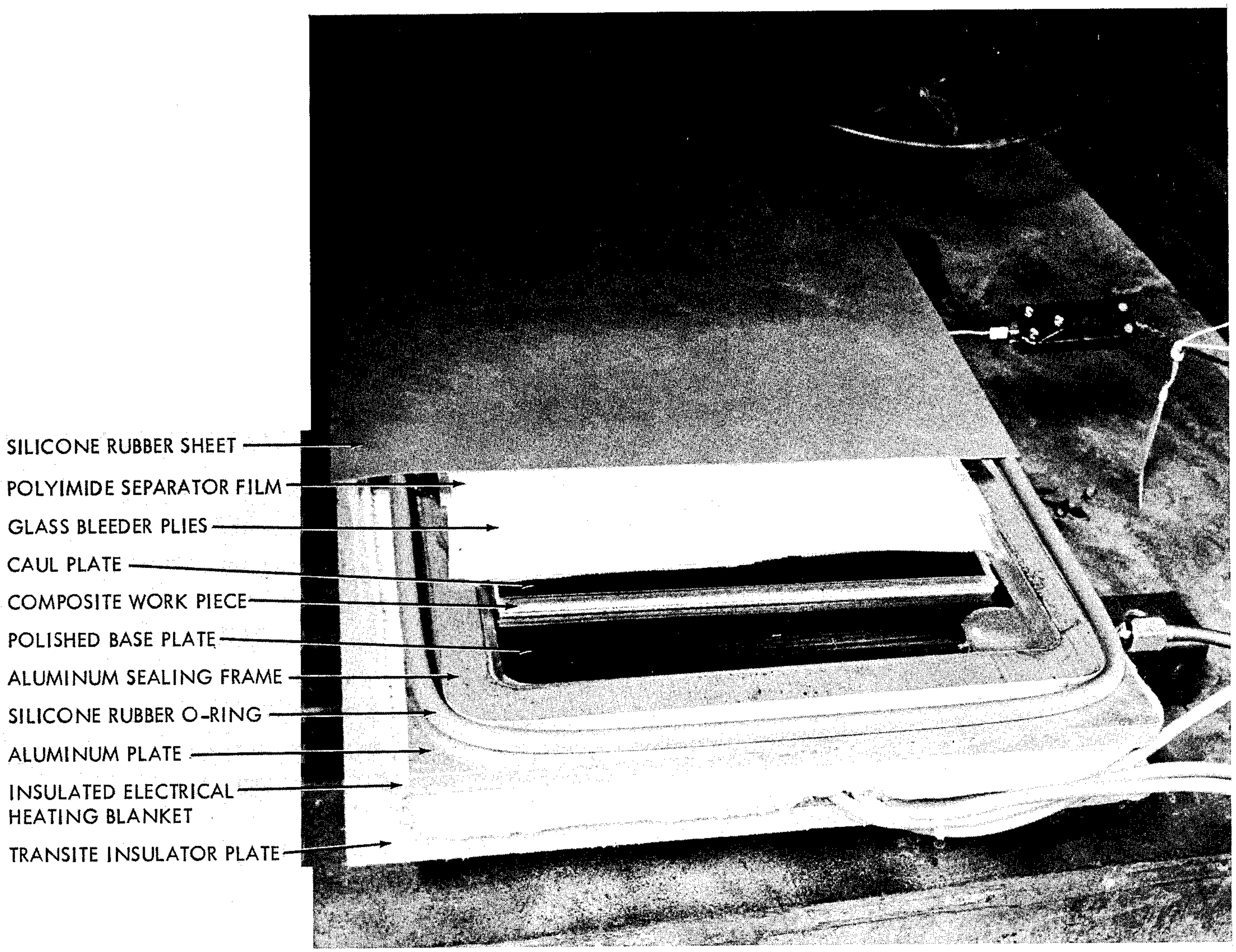


Figure 10. Photograph of Partially Complete Assembly of Locally Heated Autoclave Bag.

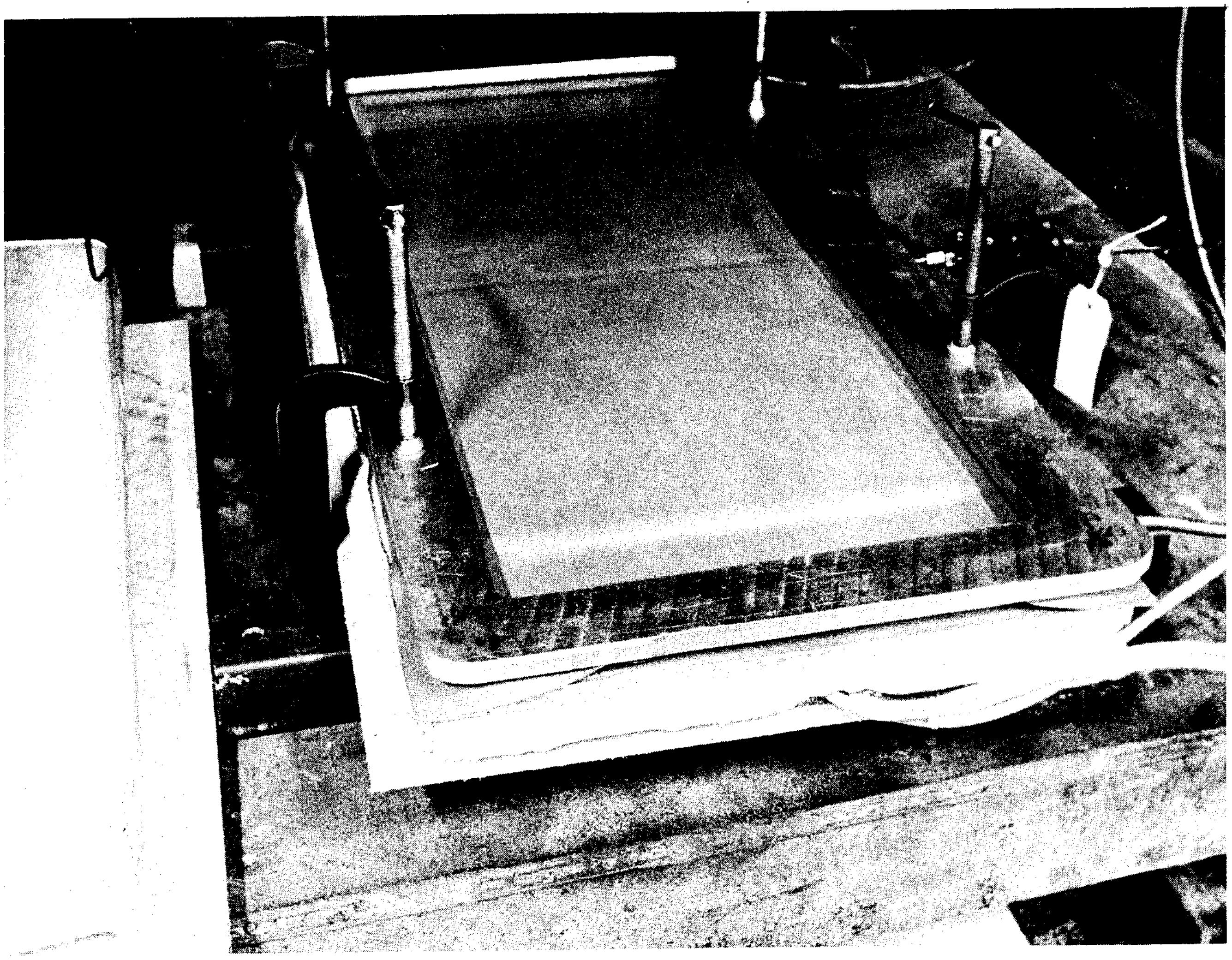


Figure 11. Locally Heated Autoclave Bag Assembly with Clamping Frame in Place and Vacuum Drawn.

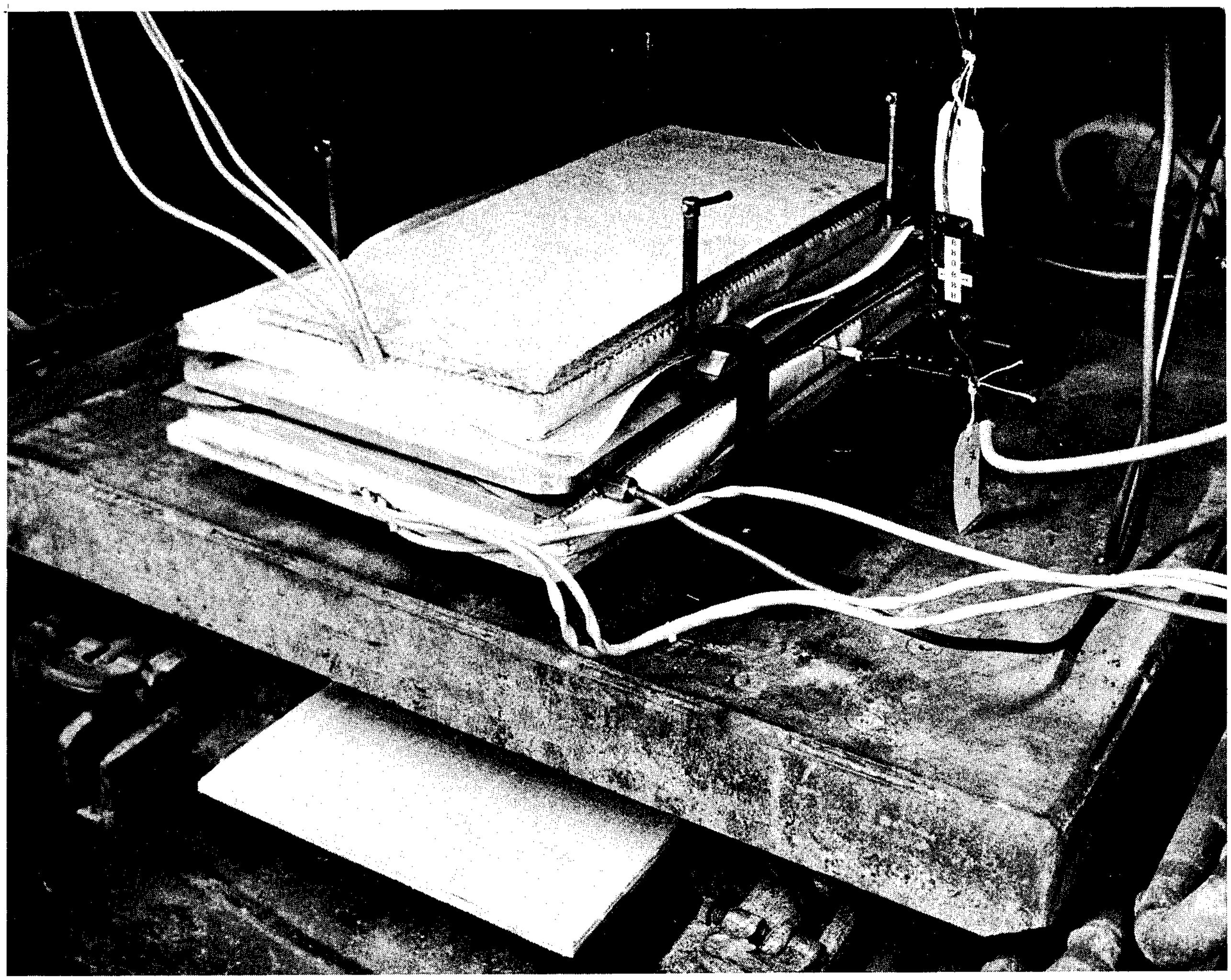


Figure 12. Locally Heated Autoclave Bag Assembly Ready to Run.

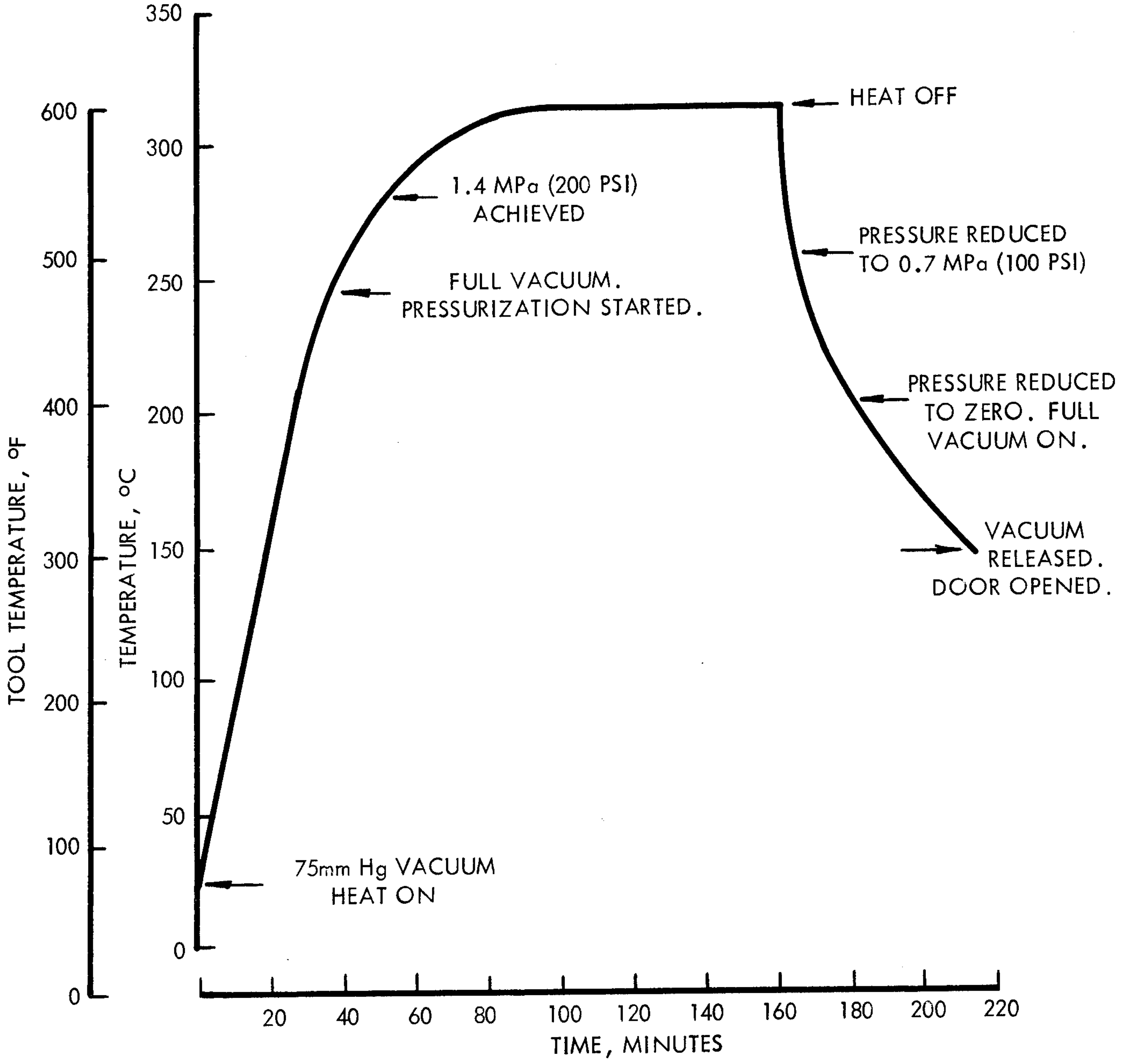


Figure 13. Typical Heating Blanket Autoclave Cycle Employed in Fabricating Laminates.

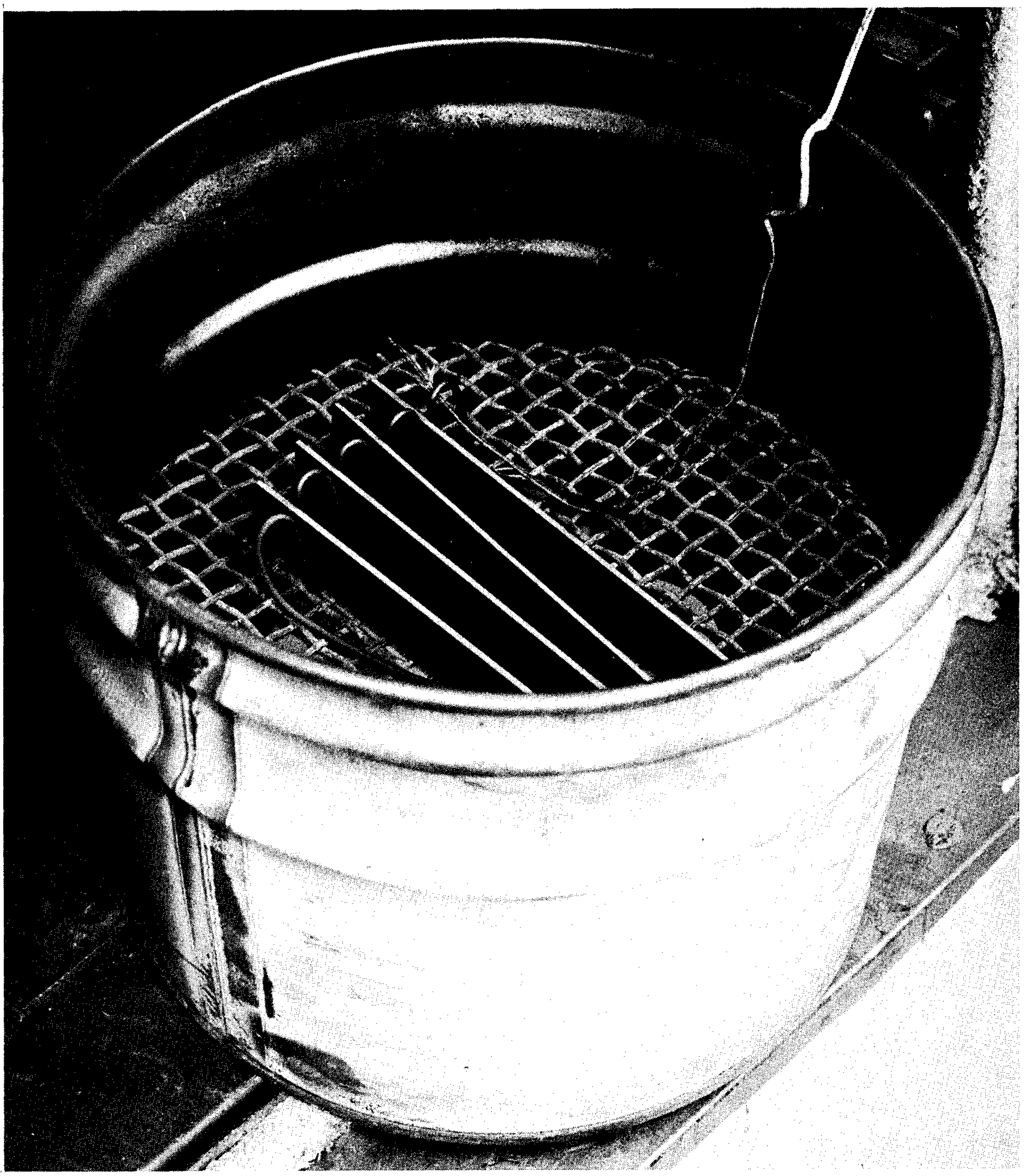


Figure 14. ITGA Specimens in Chamber Prior to Closing and Installation in Oven.

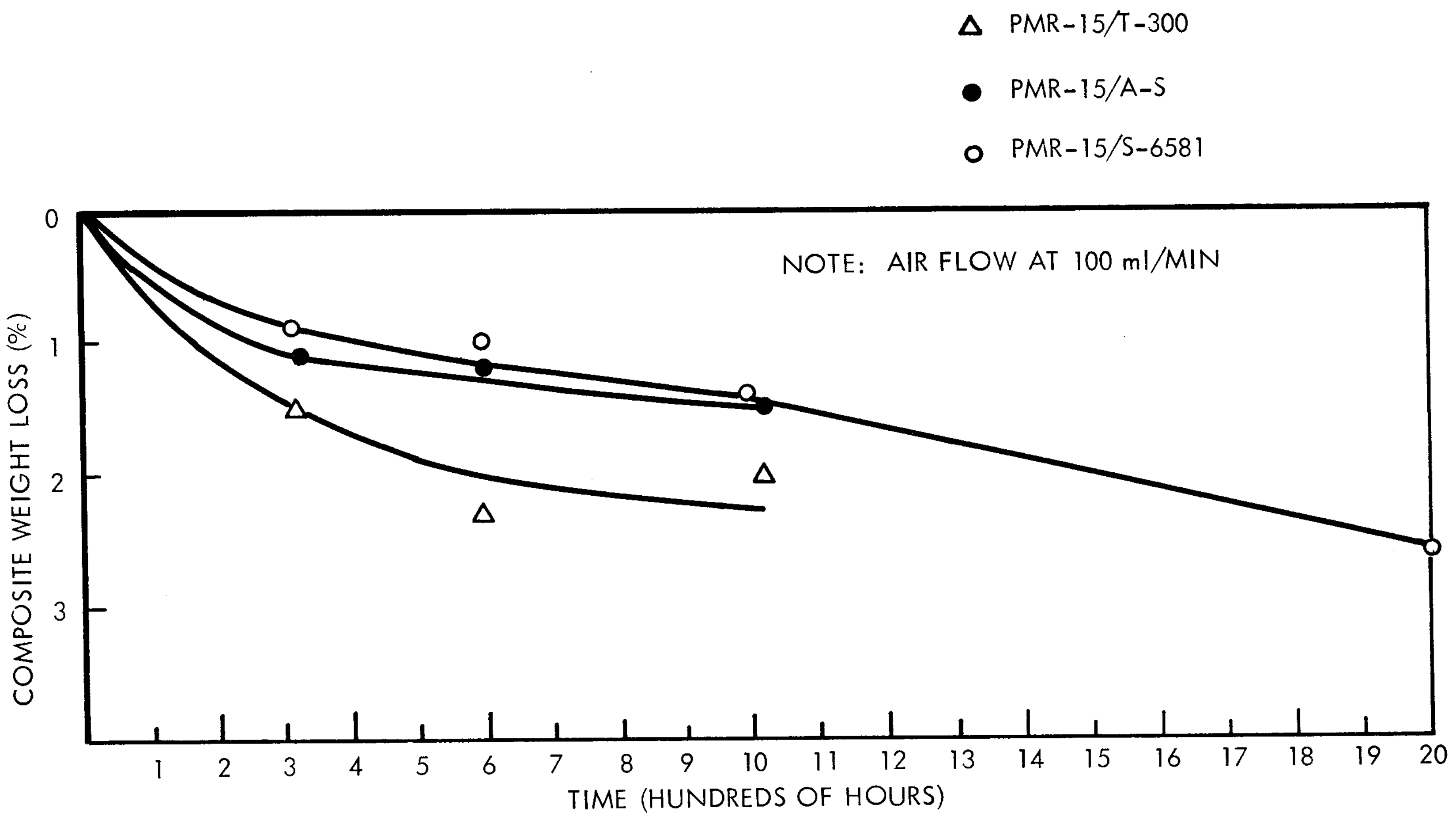


Figure 15. Weight Loss of PMR Composites at 260°C (500°F).

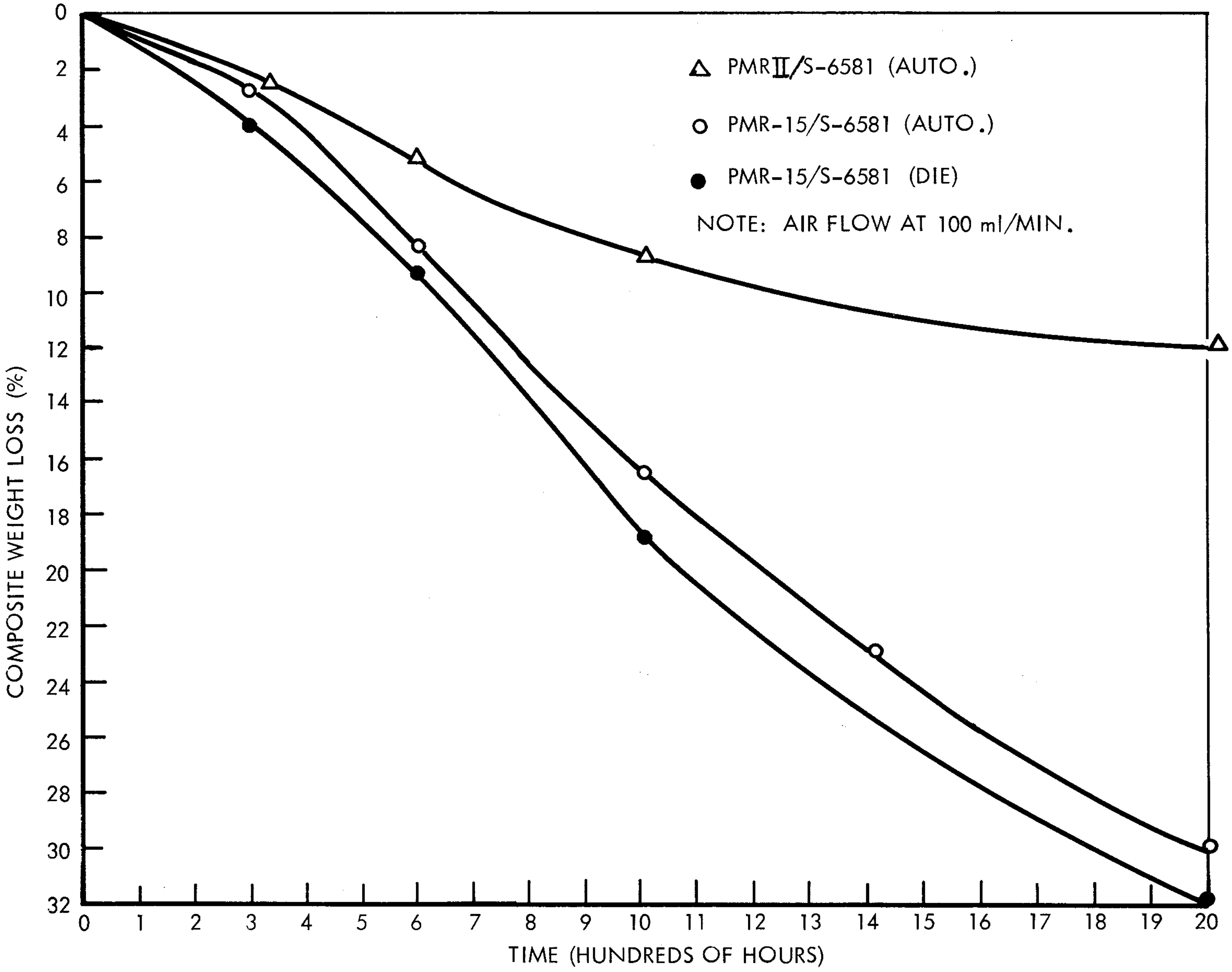


Figure 16. Weight Loss of PMR Composites at 316°C (600°F).

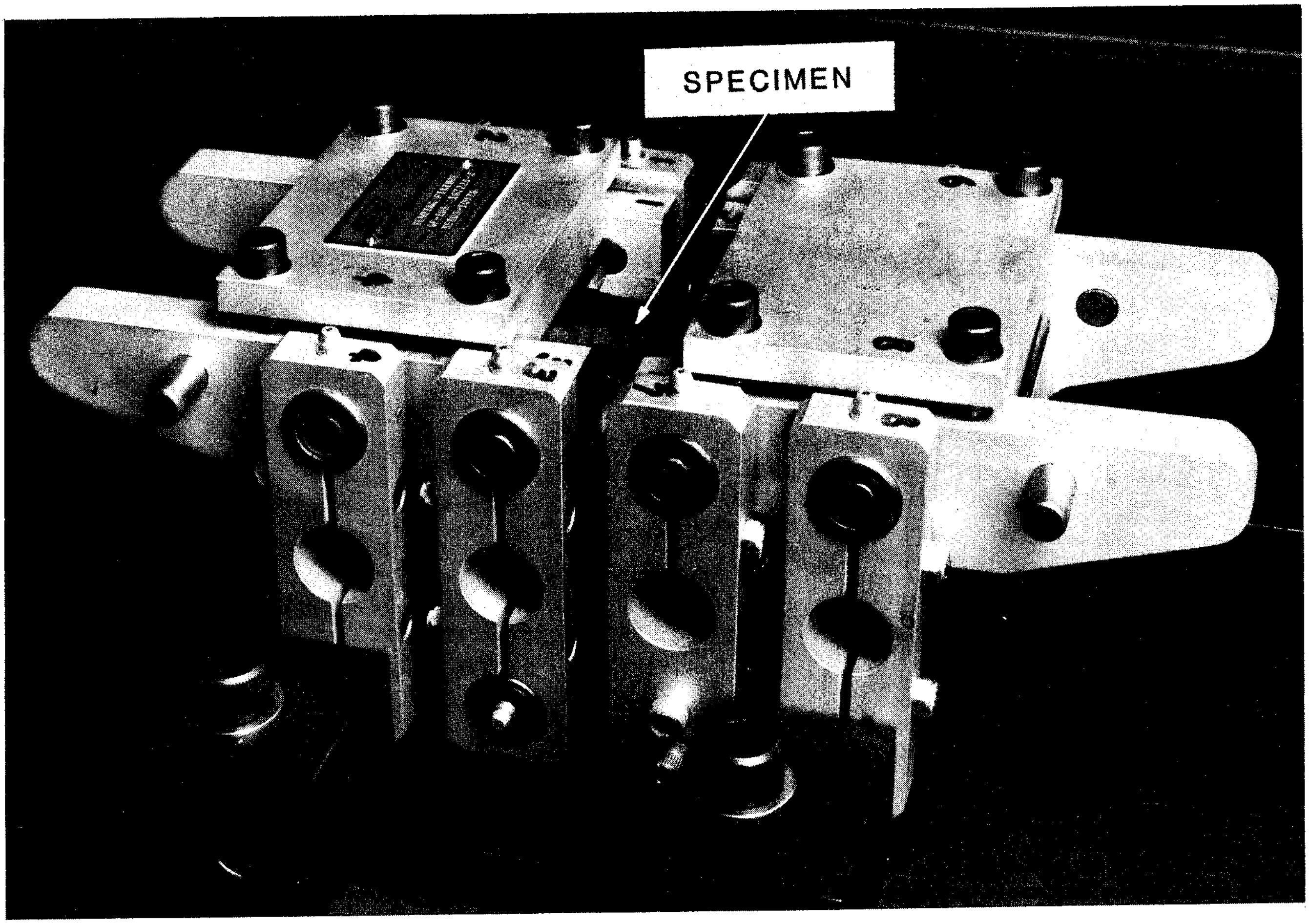
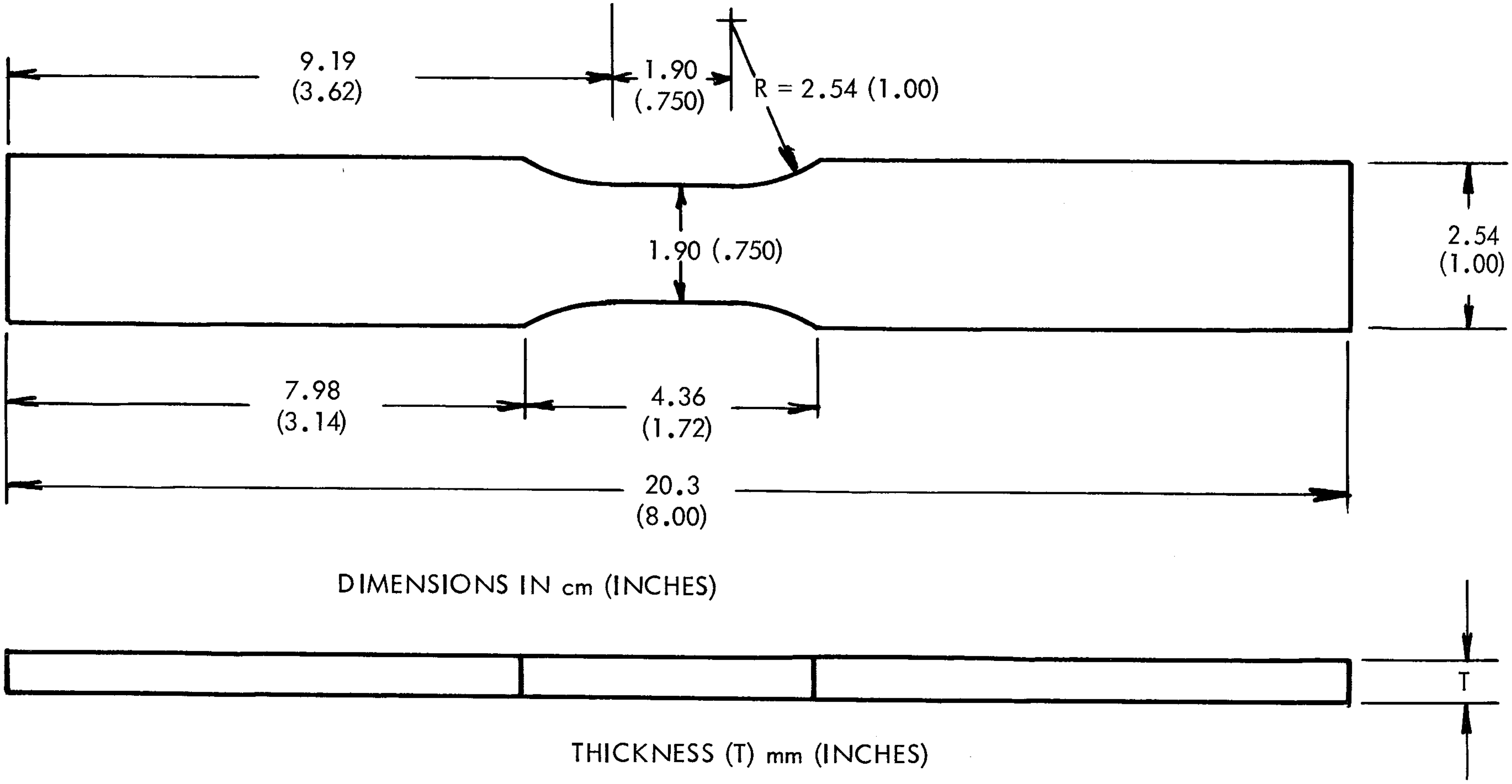


Figure 17. Reverse Bending Fatigue Fixture with Specimen in Place Mounted on Fatigue Machine.



THICKNESS (T) mm (INCHES)

A-S/PMR-15	5.72	(0.225)
T-300/PMR-15	5.64	(0.222)
S-6581/PMR-15	6.86	(0.270)

Figure 18. Reverse Bending Fatigue Specimen.

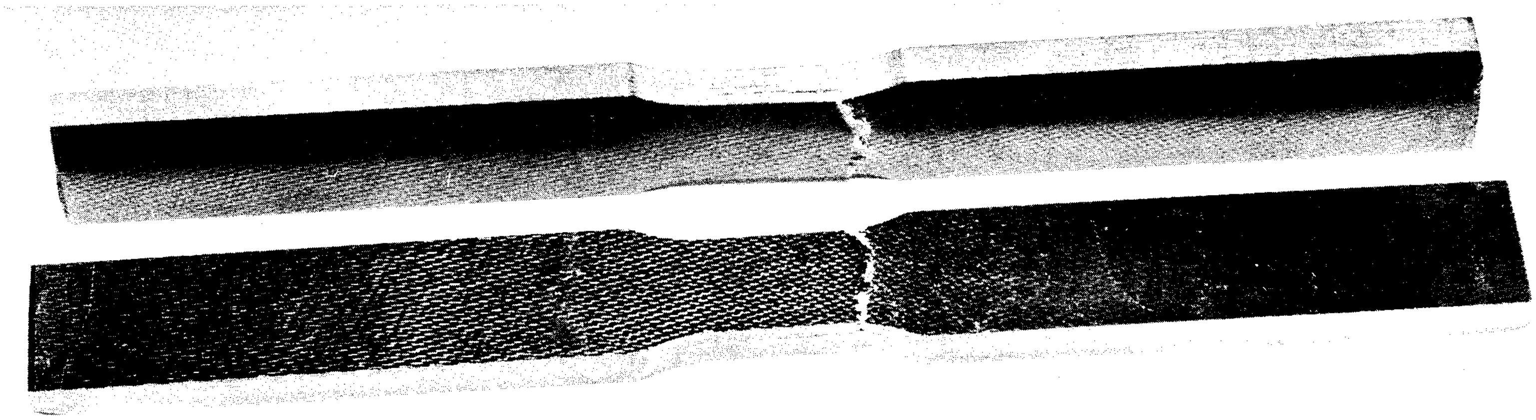


Figure 19. S-6581/PMR-15 Fatigue Specimens Showing Typical Failure Mode.

Figure 20. T-300/PMR-15 Fatigue Specimen Showing Typical Damage Locations after Test.

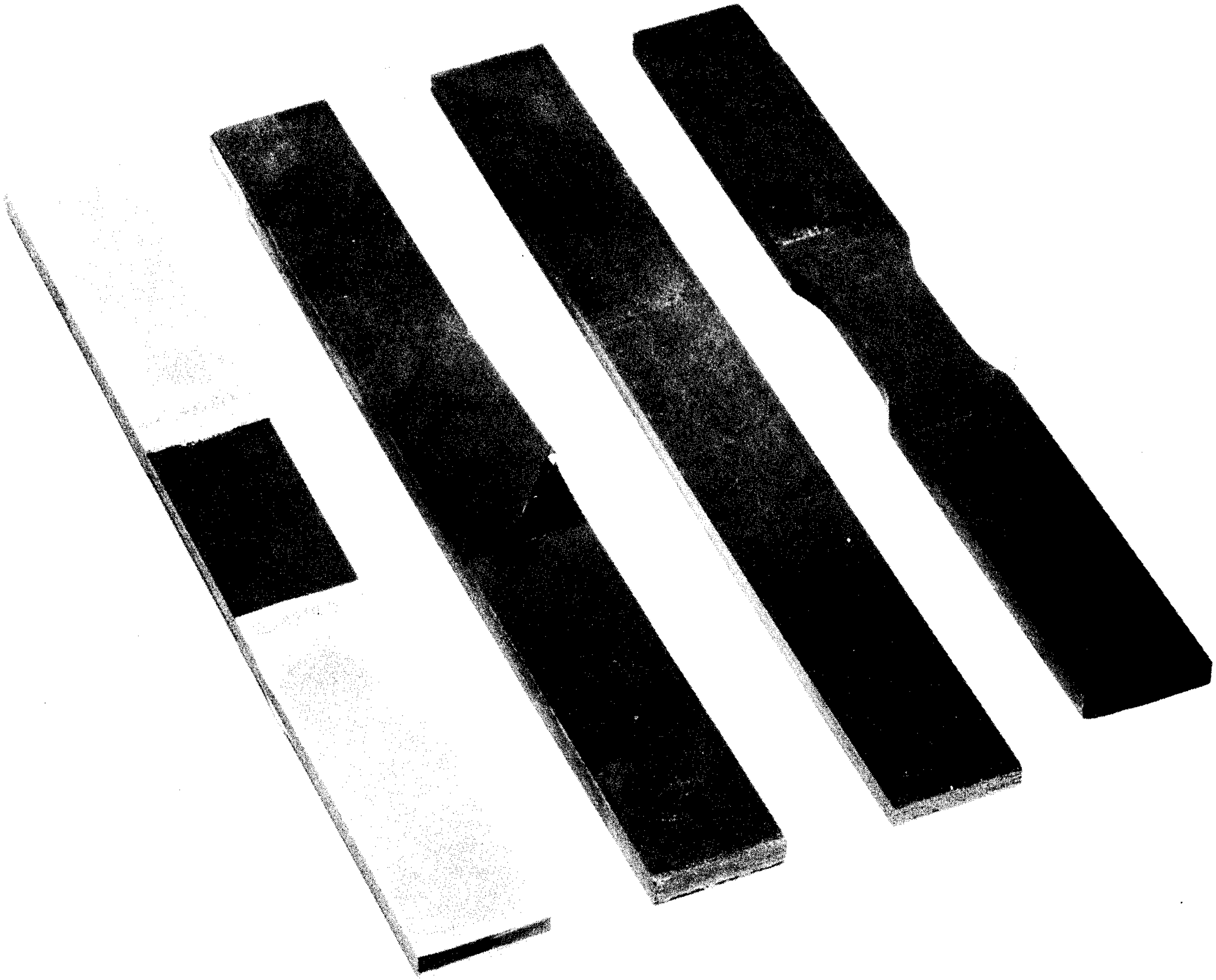


Figure 21. Four Different Fatigue Specimen Designs for A-S/PMR-15.

9583-C

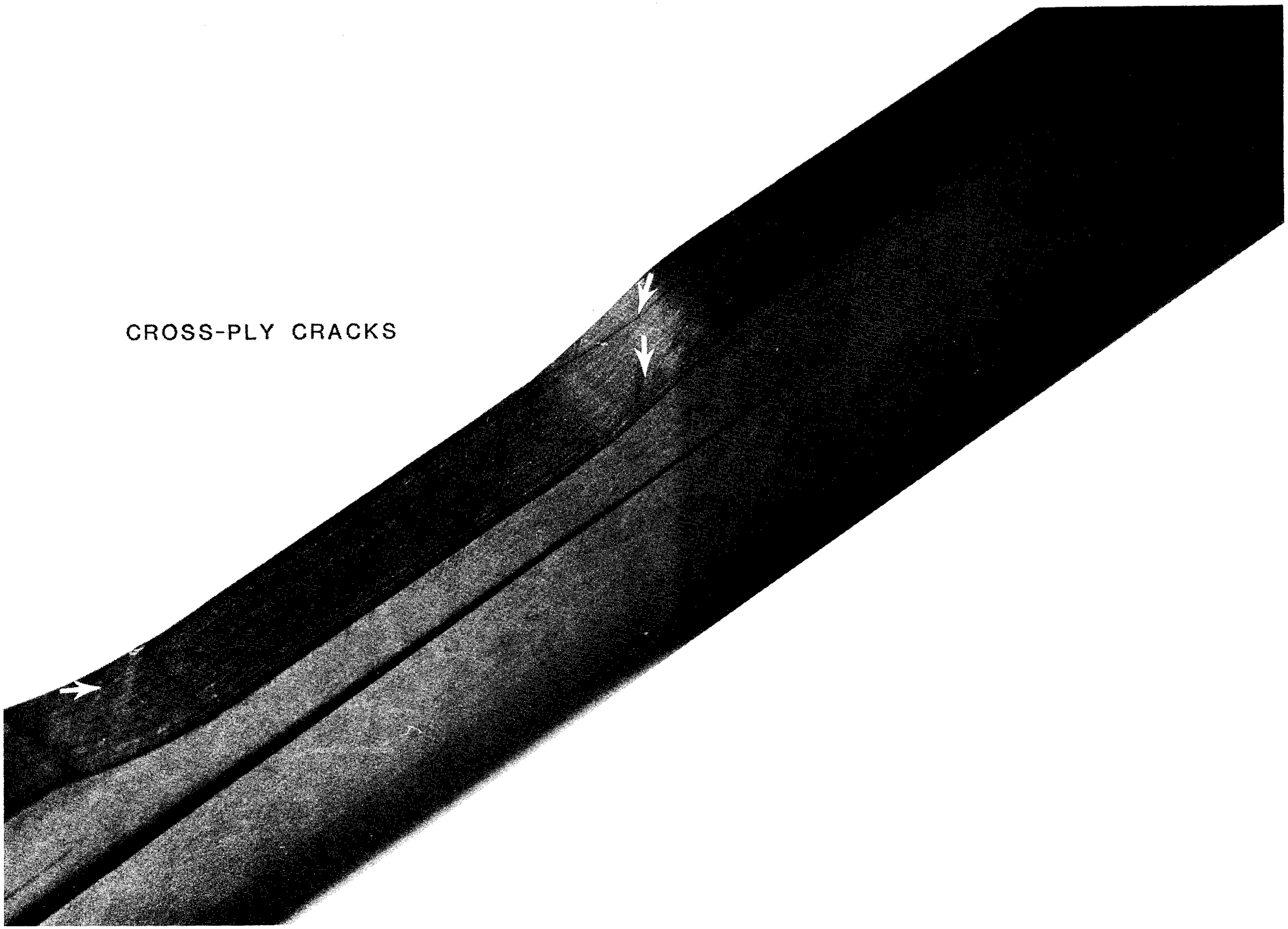


Figure 22. Magnified View of Unidirectional A-S/PMR-15 Fatigue Specimen Showing Damage Locations after Test.

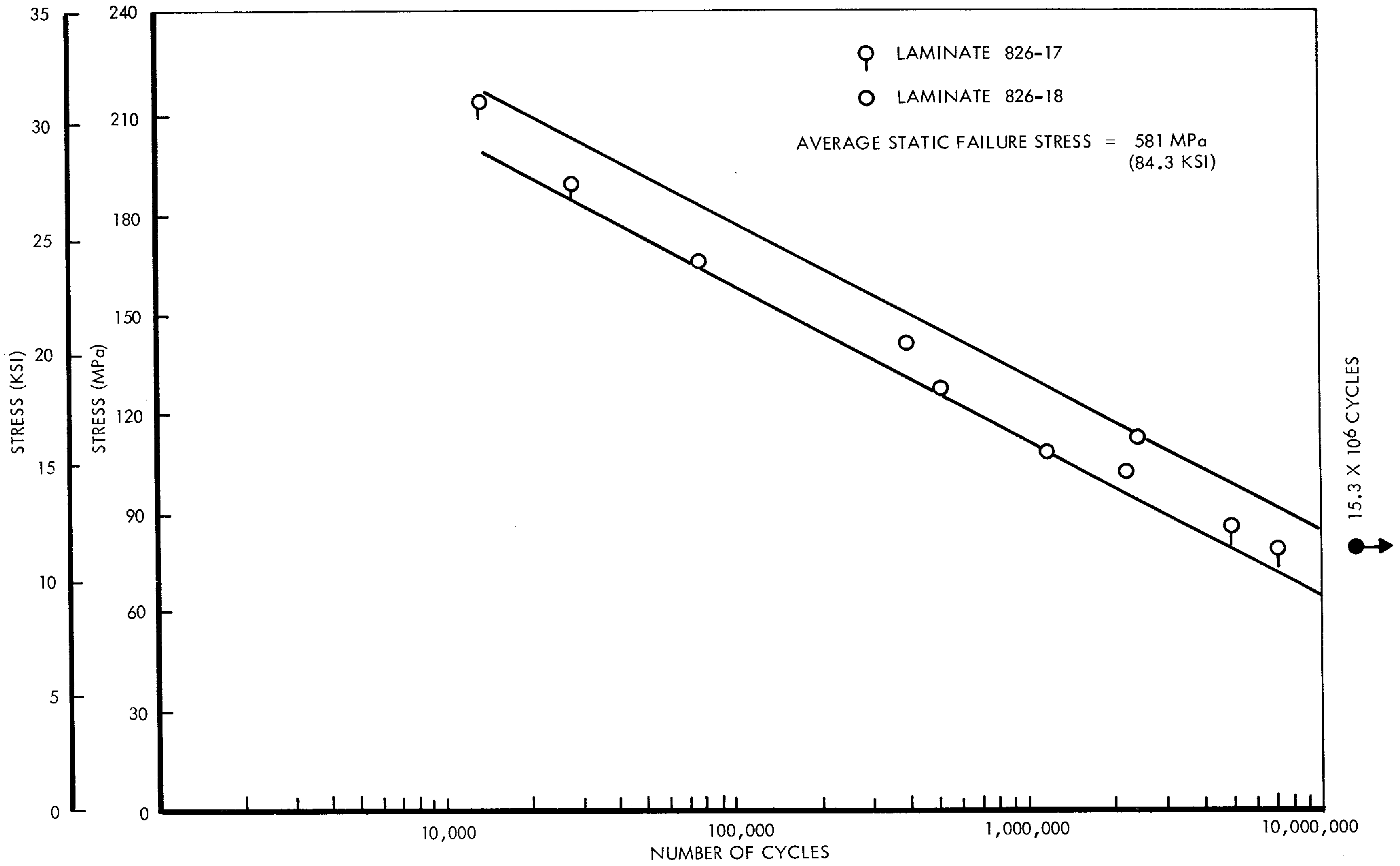


Figure 23. Reverse Bending Fatigue S/N Curve for Autoclaved Molded S-6581/PMR-15.

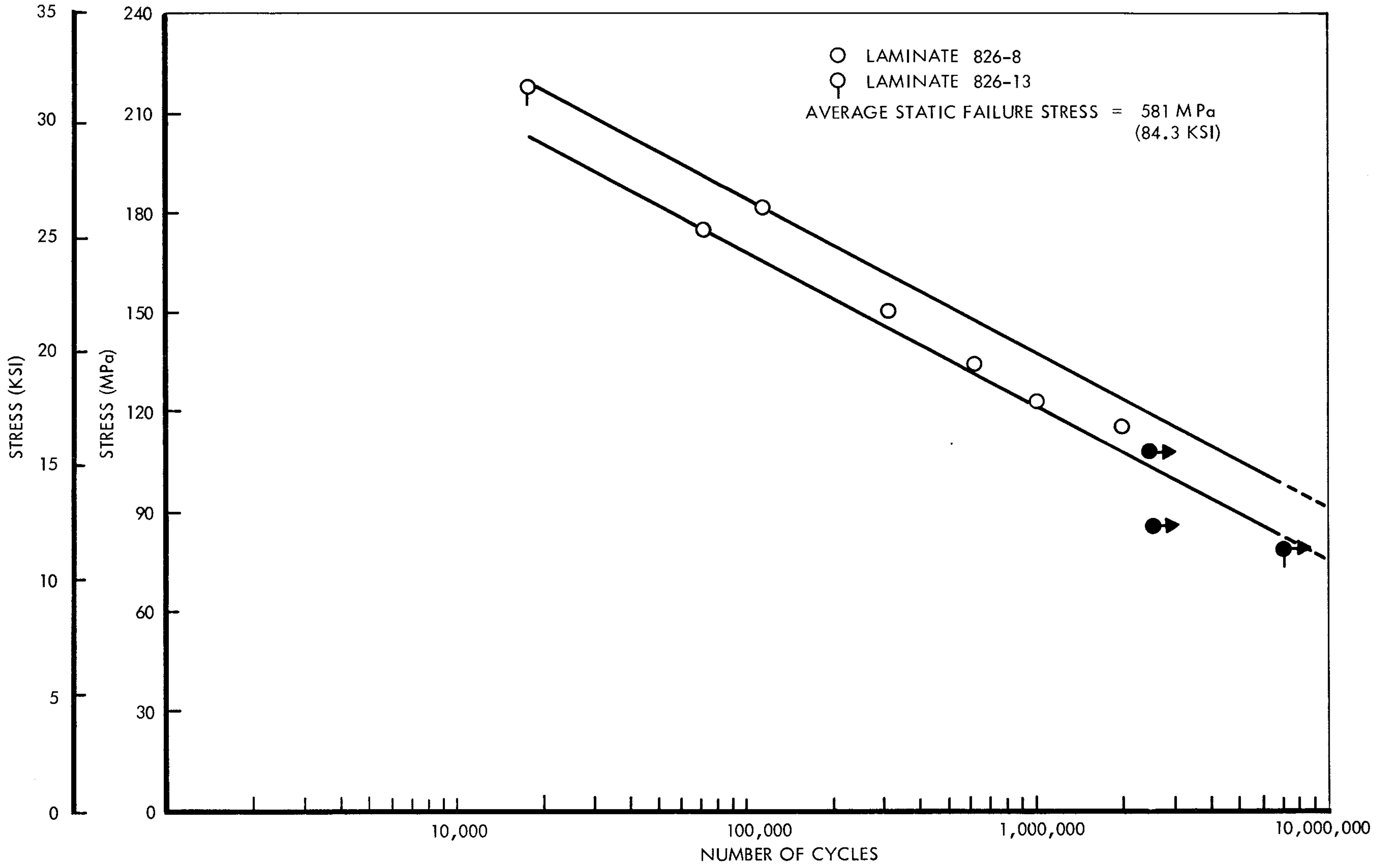


Figure 24. Reverse Bending Fatigue S/N Curve for Die Molded S-6581/PMR-15.

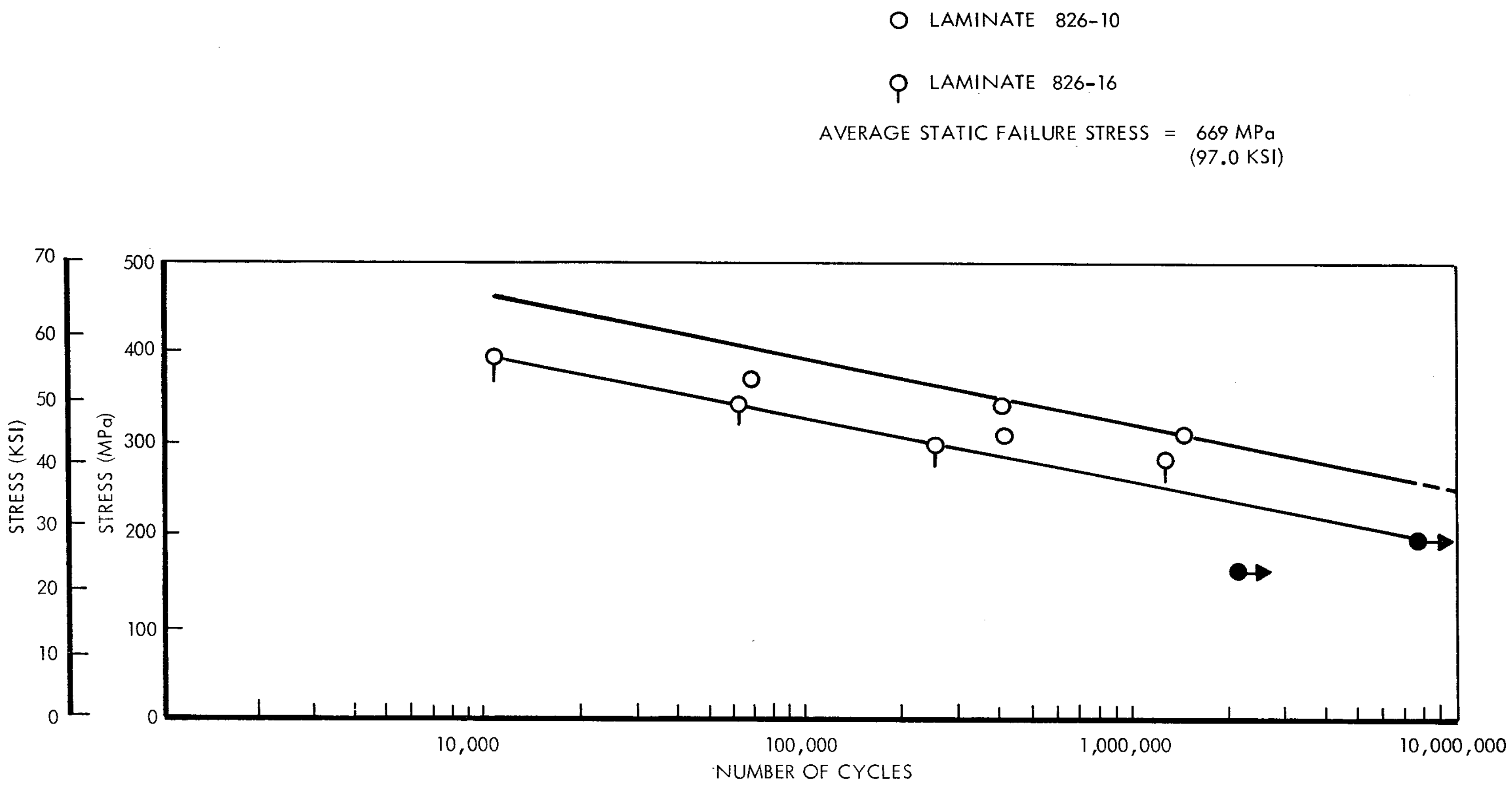


Figure 25. Reverse Bending Fatigue S/N Curve for Autoclave Molded T-300/PMR-15.

APPENDIX A

RAW MATERIAL PURCHASE REQUIREMENTS

Item #1	Unidirectional A-S/PMR-15 Prepreg. Sheet width to be 12" -0.000" +0.250" Sheet lengths to be 60" and/or 72" -0.000" +0.500"
Item #2	T-300 cloth/PMR-15 prepreg width to be 42"
Item #3	S-6581 S-Glass Cloth/PMR-15 prepreg width to be 38"

Additional requirements for each item shown in the Specification attached.

APPENDIX A (continued)

PMR-15 PREPREG REQUIREMENTS

These additional requirements apply to the designated purchase order.

Item 1: Unidirectional A-S/PMR-15

a) Fiber to be aerospace grade.

b) Fiber volume to be 59 ±1 v/o (see attached table I).

c) Total volatile content to be 13 ±2 w/o.

d) Molded per ply thickness to be 0.0075 inch ±0.0005 inch.

Item 2: T-300 Cloth/PMR-15

a) Weave to be 24 x 24 (warp and fill).

b) 3000 filament yarn.

c) Cloth to be heat cleaned to remove weaving finish.

d) Fiber volume to be 59 ±1 v/o (see attached table I).

e) Total volatile content to be 13 ±2 w/o.

Item 3: S-6581 Glass Cloth/PMR-15

a) Finish on cloth to be Burlington I-599 (formerly GB-855).

b) Fiber volume to be 58 ±1 v/o (see attached table I).

c) Total volatile content to be 13 ±2 w/o.

The following requirements apply to all three items:

a) Packaging to be vapor proof and suitable for refrigerated storage.

b) Material to be dry ice shipped marked for 0^{o}F storage.

c) Certifications required for each material which gives resin mix number, fiber, lot number, resin content, volatile content.

TABLE I

NOMINAL PREPREG RESIN CONTENTS EXPRESSED IN VOLUME AND WEIGHT TERMS

	Volume % Fiber	Weight % Cured Resin	Weight % Uncured Resin
	v/o Fiber	w/o Cured Resin	w/o Uncured Resin
Item #1 A-S/PMR-15	59	33.76	38.07
Item #2 Carbon Cloth/PMR-15	59	34.26	38.59
Item #3 Glass Cloth/PMR-15	58	27.73	31.64

Note: See attached explanatory comments.

FORMULAE AND ASSUMPTIONS USED TO CALCULATE PREPREG WEIGHT VS VOLUME RELATIONS IN TABLE I

Component Densities

PMR-15:	1.32 gm/cc
A-S:	1.799 gm/cc
T-300:	1.76 gm/cc
S-Glass:	2.49 gm/cc

Conversion from v/o Fiber to w/o Cured Resin

$$\text{Weight \& Cured Resin (CR)} = \frac{\frac{1}{\rho_f}(1-V_f)}{\frac{1}{\rho_f}(1-V_f) + \frac{V_f}{\rho_r}} \times 100$$

Where: V_f = fiber volume %.
ρ_f = density of fiber
ρ_r = density of resin

Conversion from w/o Cured Resin to w/o Uncured Resin

$$\text{Weight \& Uncured Resin (w/o)} = \frac{\frac{CR}{0.829}}{(1-CR) + \frac{CR}{0.829}} \times 100$$

Where: CR = weight % cured resin

NOTE: Since the densities for each of the fibers vary from lot to lot, it is expected that the vendor will recalculate the correct target values of w/o resin using the value for the specific fiber lot employed.

APPENDIX B

REVERSE BENDING
FLEXURE FATIGUE EQUATIONS

For a given arrangement, that is, for a given specimen length and leverage, the maximum thickness of the material (h_{max}) that can be tested is limited by the capacity of the machine.

$$h_{max} = \sqrt{\frac{3\,PR}{bs}} \text{ in inches} \qquad (1)$$

Where P = peak force, equal to the sum of the force produced by the eccentric, which cannot exceed 1000 pounds, plus preload up to 1000 pounds.

R = leverage, 3 or 6 inches.

b = specimen width in inches.

s = maximum bending stress in psi.

The minimum thickness, h_{min}, is limited by allowable motion of the reciprocating platen, ±0.37 inch for tests without preload and ±0.15 inch for tests with full preload. To calculate minimum thickness, use:

$$h_{min} = \frac{RLS}{YE} \text{ in inches} \qquad (2)$$

Where R = leverage, 3 or 6 inches.

s = repeated stress, psi.

L = free specimen length between grips, inches.

Y = amplitude of reciprocating platen motion.

E = dynamic modulus of elasticity of specimen, psi.

Equation (1), rearranged, can be used to calculate the force required to produce a certain bending stress in a flat specimen:

APPENDIX B (continued)

$$P = \frac{bh^2 s}{3\ R} \quad \text{in pounds} \tag{3}$$

Equation (2) rearranged produces a formula to calculate the amplitude of vibration of the reciprocating platen:

$$Y = \frac{RLs}{h\ E} \quad \text{in inches} \tag{4}$$

However, Equation (4) holds only for specimens of uniform width.

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2. Cavano, P. J. and Winters, W. E., "PMR Polyimide/Graphite Fiber Compostie Fan Blades," NASA CR-135113, December 15, 1976.

3. Serafini, T. T., Vannucci, R. D. and Alston, W. B., "Second Generation PMR Polyimides," Proceedings of the 21st SAMPE National Symposium, April 1976.

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8. Harris, B., "Fatigue and Accumulation of Damage in Reinforced Plastics," Composites, October 1977.

9. Mettes, D. G. and Lockwood, P. A., "The Mechanical Properties of Laminates Reinforced with High Performance Glass Fiber Fabric," Proceedings of the 21st Annual SPI Meeting.

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