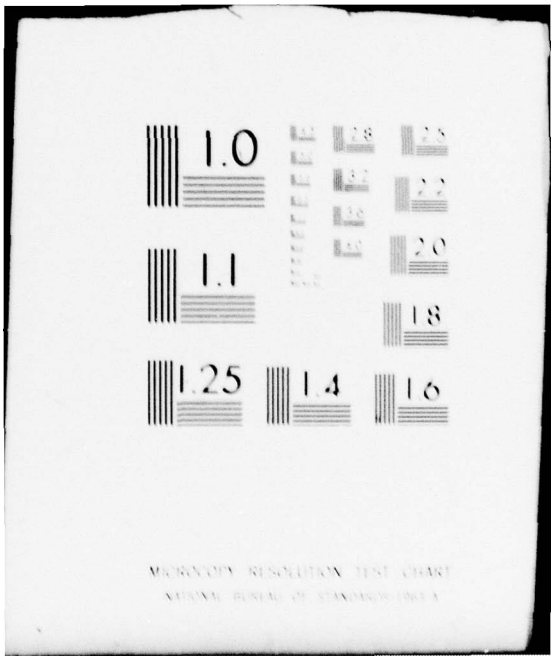
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Second Generation PMR Polyimide/Fiber Composites

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by
P.J. Cavano

PREPARED FOR...

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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project manager Raymond D. Vannucci

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16. Abstract

A second generation PMR polyimide matrix system (PMR-II) was characterized in both neat resin and composite form with two different graphite fiber reinforcements. Three different formulated molecular weight levels of laboratory prepared PMR-II were examined, in addition to a purchased experimental fully formulated PMR-II precursor solution. Investigations included isothermal aging of graphite fibers, neat resin samples and composite specimens in air at 316°C (600°F) Humidity exposures at 65°C (150°F) and 97% relative humidity were conducted for both neat resin and composites for eight day periods. Evaluation of exposed samples included room and elevated temperature testing of composites in flexure and short beam shear and tensile testing of neat resin specimens. Anaerobic char of neat resins and fire testing of composites were conducted with PMR-15, PMR-II and an epoxy system. Fire testing of composites was accomplished on a burner rig developed for this program. It was found that neat PMR-II resins exhibit excellent isothermal resistance and that PMR-II composite properties appear to be influenced by the thermo-oxidative stability of the reinforcing fiber. Humidity exposures revealed moisture absorption with an accompanying reduction of elevated temperature composite properties. The burner rig provided an inexpensive method for ranking composites for fiber release characteristics and demonstrated the existence of a relation between anaerobic char yield of the matrix and the fiber release behavior of the composites.

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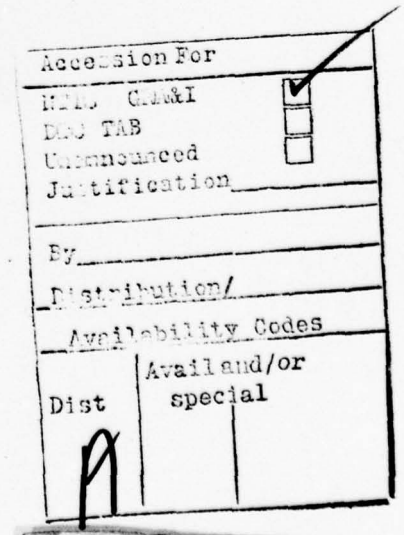
FOREWORD

This document represents the final report of the work accomplished between February 21, 1978 and June 21, 1979 by TRW Incorporated for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, under Contract NAS 3-21349 on a program entitled, "Second Generation PMR Polyimide/Fiber Composites." This program was conducted under the technical direction of Mr. Raymond D. Vannucci, NASA Project Manager.

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

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SECOND GENERATION POLYIMIDE/FIBER COMPOSITES

by

P. J. Cavano

SUMMARY

The major objectives of the program were to characterize laboratory prepared PMR-II matrices in both neat resin and composite form; evaluate a purchased experimental fully formulated PMR-II precursor solution; develop processing cycles for the composite systems; and investigate long term thermo-oxidative stability of these materials. The first generation PMR polyimide matrix system (PMR-15), evaluated by both Government and industry organizations, is now being used in significant quantities on a commercial basis. The second PMR (PMR-II) system utilizes the same cure chemistry but employs two monomers which differ from those used in the PMR-15 resin. These changes result in a polymer that was found to provide superior thermo-oxidative stability and the same ease of processing as the PMR-15. The value of characterizing the PMR-II system is therefore quite clear.

The program was conducted in three basic phases: fiber and neat resin studies, including room and elevated temperature tensile testing of three formulated molecular weight ranges of neat PMR-II after isothermal exposure in air at 316°C (600°F) and after humidity exposures for eight days; composite die molding process development; and composite evaluation including humidity exposures, isothermal gravimetric analysis, and fire testing for fiber release characteristics.

It was learned that certain PMR-II neat resins exhibit superior thermo-oxidative stability and that PMR-II composites are affected, as are other high temperature polymers, by the thermo-oxidative stability of the reinforcing fiber. A single formulated molecular weight level was selected

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as the preferred material on the basis of a balance of performance and processing characteristics. Humidity exposure revealed that moisture absorption was accompanied by a moderate reduction in elevated temperature composite properties. The experimental fully formulated PMR-II solution (purchased from an outside source) displayed acceptable properties; however, because of certain processing limitations, it was concluded that the system, in its present state of development, is not yet ready for commercial application. The fire test burner rig developed was found to provide a mechanism for the rating of composites with regard to fiber release, and a relation between neat resin anaerobic char yield and composite fiber release characteristics was demonstrated.

Further work is suggested in humidity testing of polyimides, anaerobic char and fire testing, the further pursuit of a fully formulated PMR-II precursor solution, and identification of trends and mechanisms in the isothermal testing of graphite fiber reinforced composites to define the contribution of the fiber in thermo-oxidative performance.

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1.0 INTRODUCTION

This document constitutes the final report on NASA-Lewis Contract NAS3-21349, initiated February 21, 1978, and describes the work performed between that date and June 21, 1979. The major objective of the program was to characterize the PMR-II matrix systems in both neat resin and graphite fiber reinforced composite form.

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]. A large number of government and industry organizations have evaluated the first generation PMR (PMR-15) in tests and prototype applications, and significant quantities of this material are now being used on a commercial basis.

The PMR-II matrix system employs the same chemistry of reaction but is prepared by substituting alternate monomers for two of the three used in first generation matrices. These changes result in a polymer that provides superior thermo-oxidative stability with the retention of the easy processing of the PMR-15 system[3][4].

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

Task I - Neat Resin and Fiber Studies

In Task I neat resin moldings of the PMR-II system at three different formulated molecular weight (FMW) levels were prepared and evaluated by room and elevated temperature tensile testing in the as-molded condition, after humidity exposure, and after isothermal gravimetric analysis (ITGA) at 316°C (600°F). After review of these data, two FMW levels were selected for examination in the next task. Additionally, two high-strength graphite fiber tows and a graphite fiber cloth were selected. The two tow materials were

subjected to ITGA and the more thermo-oxidatively stable identified for use in the remainder of the program. Additionally, an experimental fully formulated PMR-II precursor, identified as NR-059X, was obtained from DuPont for comparison with freshly prepared monomer solutions.

Task II - Composite Processing Studies

Using the two FMW's chosen in Task I, process cycles were developed for die molding of collimated tow prepreg and woven reinforcement prepreg. Additionally, the NR-059X was used to prepreg and mold graphite fiber laminates over a period of time to evaluate storage life. Evaluation included room and elevated temperature flexure and short beam shear testing in both the postcured and non-postcured condition. At the conclusion of this phase, the PMR-II FMW level to be used in the next Task was selected.

Task III - Development of Composite Data

Using the materials and processes identified in Tasks I and II, a series of composite laminates were prepared for evaluation. Material/process combinations included die molded unidirectional tow panels and die molded woven reinforcement panels. Evaluations included mechanical testing on these composites subjected to humidity exposures and ITGA at 316°C (600°F) out to 1500 hours. Finally, anaerobic char content of neat resins was determined and graphite fiber retention characteristics of laminates were evaluated with a state-of-the-art epoxy, PMR-15, and one FMW of the PMR-II system.

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 the PMR-II monomers and the reinforcements employed.

2.1 Resin Monomers

Two monomer solution approaches were employed to achieve a cured resin matrix. Both of these approaches are described below.

2.1.1 Freshly Prepared Monomer Solutions

As was noted earlier, the PMR-II system consists of three monomers mixed in alcohol; methyl alcohol was used throughout this program for both the preparation of methyl esters and as a carrier solvent. Figure 1 shows the structure of the three monomers used in preparing PMR-II. Table I shows the stoichiometric ratios of the three monomers for various formulated molecular weight (FMW) systems and the relation for determining FMW. For convenience, throughout this report, each system is identified with an "n" number (moles of HFDE).

The crystalline PPDA was obtained from Fisher Scientific as a Certified Reagent Grade with a melting point range of $1^{o}C$ ($1.8^{o}F$). The HFDE component was purchased in the anhydride form (HFDA) from Burdick & Jackson Laboratories, Muskegon, Michigan for esterification when needed. Burdick & Jackson separated the HFDA from DuPont's NR-050X material using the procedure described by Vannucci and Alston[5]. Figure 2 is a copy of the certification from Burdick & Jackson giving an infra-red spectrum and showing a melting point range of $2^{o}C$ ($3.6^{o}F$). Norbornene anhydride was obtained from Fisher Scientific with a $2^{o}C$ ($3.6^{o}F$) melting point range for later esterification. The anhydrous methyl alcohol was purchased from Fisher Scientific.

Standard procedure for the preparation of monomeric reactant solutions for prepregging includes separate esterification of both the HFDA (two hour reflux time) and norbornene anhydrides (three hour reflux time) with anhydrous methyl alcohol in 50 w/o concentrations and combining these with PPDA and enough alcohol wash to produce a final 50 w/o solution. Prepared in this

manner, a cured resin solids concentration of 41.2 w/o is realized. In preparing material for neat resin molding, this solution is put through a Buchner filter to eliminate any chance particulate matter that would subsequently create a stress concentration point in test specimens. Once the three monomers had been combined, the combined solution was used that same day. The need for this precaution has been recently confirmed by Lauver, et al[6].

In selecting the FMW's for study, a number of factors were considered. Serafini and Vannucci[7] showed, with PMR 15, that formulated molecular weight can modify thermal stability, both short and long term, and processing characteristics. A low FMW yields high flow values for ease of processing. However, a low FMW can reduce long term thermo-oxidative stability. If a very high FMW were chosen, flow in molding could be reduced although long term stability would be good. If the FMW were taken too high, it seemed possible that a thermo-plasticity effect could be observed at high use temperature without excessive postcure. The problem then was to identify a FMW range over which the best balance was maintained among fabrication ease (with various processes), long and short term high temperature performance characteristics.

In Reference 3, two FMW's were examined; n = 1.67 and n = 2.00. Little difference was noted in composite mechanical properties or oxidative stability. On NAS3-20366[4], TRW performed limited studies with n at 1.67. It was therefore decided to study a wide working range on the program by investigating FMW's of 1262 (n = 1.67), 1690 (n = 2.50) and 1071 (n = 1.30). In this way, it was hoped to clearly define a useful range applicable for multiple processes with a good balance of properties.

2.1.2 Fully Formulated Solution

A limited evaluation, in both neat resin and composite form, was conducted on a DuPont matrix system designated NR-059X. This is an experimental, fully formulated PMR-II precursor solution. It was felt that, if the NR-059X system were equal to the freshly prepared monomer solutions, it would be

advantageous to have a pre-mixed fully formulated system available on a commercial basis. The NR-059X (Lot E-15588-66) was shipped packaged in dry ice. Upon receipt the material was stored at -18°F (0°F).

2.2 Fiber Reinforcements

The following paragraphs discuss the rationale used to select the high strength fibers for program use and the test of their isothermal performance.

2.2.1 Initial Candidate Selection

In Task I of the program, selection was to be made of two candidate high strength graphite unidirectional fiber tow materials. Recent work from several sources has revealed that the oxidation resistance of high strength graphite fibers is extremely variable. It has also been shown by Gibbs, et al[8], among others, that the thermo-oxidative stability (TOS) of a composite is directly related to the TOS of the reinforcement (figure 3). It was therefore desirable to select a reinforcement for the evaluation of PMR-II composites which would minimize the effects of the reinforcement as much as possible.

In a recently published report, Sheppard[9] has shown that Thornel 300 and Hercules HTS-2 are severely affected after 593 hours at 316°C (600°F) (table II) while Modmor II is little affected under these conditions and Celion 3000 is somewhat intermediate in TOS performance. However, Modmor II fiber is no longer available. Gibbs[8] found a similar spread in TOS among several materials evaluated and found Great Lakes Fortafil 3 approximately equivalent to Modmor II (table III) after 700 hours at 316°C (600°F). It is interesting to note that untreated Fortafil (F-3U) exhibited almost complete degradation under these conditions. McMahon[10] at Celanese found that, of the high strength fibers tested after 3 hours at 773°C (1423°F), AS, Panex 30A, Modmor III and Thornel 300 were almost completely consumed while Celion 3000/6000 materials lost only 3-5% of their weight. The Hercules HT-S exhibited considerable variability in performance. These data are shown in table IV.

Based on the information discussed above, the two high strength graphite fiber tow materials selected for further examination were the Fortafil-3 and the Celion-6000. Both are derived from polyacrylonitrile (PAN) precursors, surface treated for shear improvement, and are available with an epoxy size. The F-3 material was obtained in a 40,000 filament tow from Great Lakes Carbon Corporation, New York, New York, and the Celion-6000 from the Celanese Corporation, Chatham, New Jersey. Typical fiber properties, as reported by the respective vendors, are shown in tables V and VI.

2.2.2 Fiber Isothermal Studies

Small quantities of each of the two fiber tow materials were obtained with an epoxy size for isothermal gravimetric analysis (ITGA). The Fortafil-3 was designated as lot CT #5511 and the Celion-6000 was from lot HTA-7-6911.

Triplicate samples of fiber of approximately four grams each were loosely coiled, secured with a stainless steel wire, and placed in stainless steel pans. All six pans were then put into a 14 liter chamber within an air circulating oven and preheated, bottled air metered into the chamber at 100 ml/min. Temperature was monitored with a thermocouple inside the 14 liter chamber, and the temperature adjusted to 316^{o}C (600^{o}F). All samples were periodically removed and weighed. Figure 4 shows an overall view of the ITGA oven and figure 5 shows a closeup of the fiber samples ready for placement in the ITGA chamber.

Weight loss values vs. time out to 1000 hours are plotted in figure 6. In both cases, the weight loss after 24 hours was 1.2%. This value, it is felt, represents the epoxy finish applied to both tow materials. As can be seen from the curves, the Celanese material shows slightly less weight loss out to about 500 hours when the curves cross. The percent loss on the Celanese is consistent with the data reported by Boeing[9]. The Fortafil data show a greater loss than reported in reference 8, but the general trend, that is, the Fortafil-3 as more resistant than the Celanese, is confirmed. The absolute weight loss value obtained, compared with other values reported, is a function of test method and specific lot examined.

Mr. B. H. Eckstein has indicated[11] that the total carbon content of the fibers is extremely important; he has reported that only fibers with a carbon content of over 97% survived 1000 hours at 375°C (707°F) in a series of tests in his laboratory. The reported nominal value on the F-3 fiber is 96.5% carbon; McMahon of Celanese has reported the carbon content of the Celion 3000/6000 material to be 93.0%. These data are consistent with the greater loss shown by the C-6000 tow material shown in figure 6.

Another characteristic noted with the two fiber materials, after a 1000 hour ITGA exposure, was the differential weight gain noted after ambient retention for five hours. Table VII lists the values collected on the triplicate fiber specimens. The F-3 fiber picked up 0.8%, while the C-6000 samples showed an average weight pickup of 8.7%. This is apparently due to resorbed gases on the oxidized fiber surface, but the phenomenon is not well understood. It is not clear, in this case, whether the difference in weight pickup is due to variation between the two carbon fiber surfaces or to relative extent of the damage done to the surface by the previous ITGA exposure.

2.2.3 Program Reinforcements

Based on the information discussed above, it was decided to use the F-3 tow material for unidirectional laminate studies. A second lot of the F-3 was obtained for use with the composite studies portion of the program. This was lot RS-885 and was obtained without the epoxy size.

Selection was also to be made of either S-glass or a graphite fiber fabric for composite characterization. It was observed in a previous program[4] that certain PMR/S-glass composites experienced an accelerated degradation at 316°C (600°F) when compared to graphite fiber reinforced PMR composites. The reason for this behavior is not known at this time, but to make the comparisons to the unidirectional composite evaluations more valid, it was decided to choose a graphite fiber fabric for study. Currently, the two most common woven graphite fiber fabrics in the industry are prepared from T-300 and C-3000. Based on the data discussed above, it was decided to select the C-3000 woven graphite fiber material. This fiber is the same as the C-6000 except fewer filaments are used in each tow.

The C-3000 tow was woven by Prodesco, Incorporated, Perkasie, Pennsylvania into a 8-Harness satin construction with 23 x 22 tows per inch in the warp and fill direction, respectively. This fabric corresponds to the most common configuration of T-300 cloth in the market. The cloth was approximately 24 inches wide and had the same epoxy size as was used in the unidirectional tow material.

3.0 NEAT RESIN STUDIES

The sections below describe the investigations performed with the unreinforced resin matrix systems; both the freshly prepared PMR-II and the fully formulated precursor from DuPont. Included are discussions of both fabrication and characterization studies.

3.1 Neat Resin Molding

The molding techniques used for both the freshly prepared PMR-II and the NR-059X system are described below.

3.1.1 Freshly Prepared Monomer Solutions

As was noted in paragraph 2.1.1, the freshly prepared monomer solutions were prepared in methyl alcohol at a 50 w/o concentration and filtered. After filtration the solutions were dried in an air circulating oven at 82°C (180°F) for 72 hours. During drying the beakers containing the solution were covered to avoid contamination by air borne impurities. The dried material was then broken into pieces, imidized for two hours at 204°C (400°F) and ground into a fine powder using a mortar and pestle.

The imidized powder was put into a cold die, which was then placed into a press between heated platens. About 10% excess molding powder was used to provide resin flash for checking fluidity during molding. Stops were used to prevent complete expulsion of the resin during its viscosity drop. When the extruded flash reached gelation, the stops were withdrawn and pressure reapplied. A number of different heat-up cycles were examined. If the heat-up rate was too slow, the molded panel exhibited a grainy appearance with very little strength until after postcure at 316°C (600°F). The cycle shown in figure 7 gave good quality moldings on a reproducible basis (20.6 cm x 20.6 cm with a nominal thickness of 1.5 mm), with material having n values of 1.30 and 1.67.

The quality, as indicated by a visual examination with light transmitted through the molding, was good. However, with one exception, all of the moldings were cracked into a number of pieces when removed from the die.

The problem was identified as the large differential thermal expansion between the tool and the neat resin molding which caused cracking as the panel cooled in the die. A number of cooling techniques were tried with variations in retained pressure. The only process cycle that was successful was removing the moldings hot. At the end of the 316°C (600°F) hold, all pressure was removed and the part removed at 316°C (600°F). This technique, while physically awkward, resulted in sound, one-piece moldings.

The molding cycle used to obtain sound pieces of PMR-II with n's of 1.30 and 1.67 is shown in figure 7. This was identified as the A cycle. The same cycle was also used to prepare neat resin moldings with an n of 2.50. However, panels molded with this cycle were unacceptable. Surfaces exhibited a very rough surface full of depressions and what appeared to be blisters. Attempts with an n of 2.25 displayed the same effects. Figure 8 shows a panel (n = 2.50) with the defects described.

To eliminate these defects, an alternate cycle was devised. Temperature rise-rate was the same as that shown in figure 7, but pressure was applied immediately after the cold die was placed in the 316°C (600°F) preheated press platens. Pressure was maintained until flow was visually observed at the die edges; this occurred in 11.5 minutes with the n at 2.50. At the observation of flow, pressure was released and held in this condition for 10 minutes. After 10 minutes, the stops were removed, the pressure reapplied, and the molding held for three hours under pressure at 316°C (600°F). This procedure was identified as the B cycle. This same B cycle was then also used successfully in preparing two other PMW panels, n = 2.25 and n = 1.67. It is interesting to note that flow was observed at 7 to 8 minutes with n = 1.67 and 10 minutes with n = 2.25 compared to 11.5 minutes with the 2.50 system. With all three PMW's, void-free panels, determined by visually examining the panels against a back-light, were produced.

The 316°C (600°F) hold period was extended from one hour to three based on postcure weight loss results observed on panels molded with the two cycles described. On three pa ls (21.5 x 21.5 cm) weight losses in a 16 hour postcure at 316°C (600°F) were as follows:

n	Die Hours at 316°C	Weight Loss % in Postcure
1.30	1	2.8
1.67	1	2.4
2.25	3	0.9

It was felt the large comparative weight losses experienced with molding held one hour were excessive and indicated the longer hold time at 316°C was required.

After postcure specific gravities were determined, by water immersion, on three different FMW's. It was noted that the values increased with FMW. This would correspond to the increasing amounts of the higher density fluorine bearing monomer, as shown below:

n	Sp. Gr.	w/o HFDE
1.30	1.41	50.7
1.67	1.42	55.5
2.50	1.43	62.2

3.1.2 Fully Formulated Precursor Solution

As was noted in paragraph 2.1.2, an experimental, fully formulated PMR-II precursor solution was obtained from DuPont; this material is designated NR-059X and will be identified throughout this report in that manner to distinguish it from the freshly prepared monomer solution approach. The material was received in a carton packed with dry ice. A small sample was held out at room temperature and the remainder stored in a freezer at -18°C (0°F). The sample at room temperature precipitated after eight days. The material in the freezer showed no visible precipitation after two months, after which observation was discontinued.

To compare NR-059X moldability with PMR-II made from freshly prepared monomer solutions, a number of neat resin moldings were made. Using the same techniques described above for preparing an imidized molding powder, the NR-059X was dried, broken up into pieces, imidized and ground in a mortar and pestle. Initial attempts to mold panels resulted in blistered pieces when the

same "B" molding cycle employed with PMR-II was used. Good results were finally obtained when a series of "bumping" or "breathing" intervals were introduced.

The molding cycle used to successfully fabricate the NR-059X material used the same temperature rise cycle shown in figure 7. Pressure was applied immediately at the time of insertion of the die into the preheated platens (316°C) and held for 10 minutes. At the end of this time, pressure was interrupted momentarily and reapplied for a five minute hold. Following this a series of one minute pressure applications alternated with short pressure reliefs were continued until the free floating punch no longer showed signs of lifting when the pressure was relieved; there were typically seven of these "bumping" steps. At the end of this series of steps, the mold stops were removed and the full pressure reapplied and held during a three-hour hold at 316°C (600°F). This cycle was used to successfully mold sound panels 10.4 cm x 10.4 cm (4 x 4 inches) with a nominal thickness of 1.5 mm (0.060 inch). Specific gravity of the moldings after postcure was 1.41.

The postcure employed was the same as for the PMR-II moldings, 16 hours at 316°C (600°F). As can be seen from the data shown below, the NR-059X showed high weight losses in postcure even after three hours in the die, when compared to the freshly prepared PMR-II.

Neat Resin Weight Loss in Postcure

PMR-II n	Die Hours at 316°C (600°F)	Weight Loss % in Postcure
1.30	1	2.8
1.67	1	2.4
2.25	3	0.9
NR-059X	2	3.8
NR-059X	3	3.5

The NR-059X material clearly required a modified cycle from the PMR-II, seemed to react more slowly, and evolved gases over a longer interval during molding. It could not be determined whether these evolved gases were condensation reaction products from the imidization cyclization or unreacted cyclo-

pentadiene from the reverse Diehls-Alder cross linking reaction.

3.2 Neat Resin Characterization

Using neat resin moldings prepared in the manner described above, physical and mechanical property determinations were conducted on various formulated molecular weight PMR-II systems. Evaluations included anaerobic char content, glass transition temperatures and tensile properties before and after isothermal exposures and humidity conditioning.

3.2.1 Isothermal Gravimetric Analysis Testing

Isothermal gravimetric analysis (ITGA) testing at 316°C (600°F) for 1000 hours was performed on neat resin moldings of PMR-15 and three different formulations of PMR-II; these had n values of 1.30, 1.67 and 2.50. Weight changes were measured on duplicate coupons approximately 2.5 x 5.0 cm (1 x 2 inches). In addition to the weight coupons, eight sets of triplicate tensile specimens of each of the three PMR-II systems were inserted in the ITGA chamber shown in figure 4 and described in Section 2.2.2. Calculation of nominal surface area-to-weight ratios for the placques and the tensile specimens showed them to be roughly equivalent. The placques had a value of about 10.0 cm^2/gm and the specimens 10.6 cm^2/gm.

Groups of tensile specimens were secured inside envelopes of fine mesh 316 stainless steel screening (70% open) and stacked one upon another with a small weight on top of the stack. This stack was rested on open stainless steel honeycomb to permit air flow up through the packages onto the specimens. Specimens were provided for triplicate tensile test of each formulated molecular weight at room temperature and 232°C (450°F) after each exposure time, for comparison with baseline data collected on unexposed specimens.

Figure 9 is a plot of neat resin weight loss for the three different PMR-II systems against the PMR-15. As anticipated, the three PMR-II materials show an increasing weight loss with the decrease in n values. The difference in performance can be attributed to either the decrease in alicyclic content with increasing n values, or to the increase in imide ring

content as the alicyclic content decreases[5].

Figure 10 shows the average combined length and width change experienced by the neat resin moldings during the ITGA exposure. It is worth noting that the PMR-15 shows the greatest change compared to any of the three PMR-II systems examined.

As was noted above, tensile specimens were withdrawn for test from the ITGA chamber at four intervals during the 1000 hour exposure. Figure 11 is a schematic of the specimen showing the dimensions; figure 12 is a photograph of the specimen ready for test. Strain gage extensometers were used with room temperature specimens to collect strain data for calculation of moduli and elongation values. Elevated temperature specimens were run in a specially constructed oven inserted between the grips of the Instron Tensile Tester. The heated chamber of the oven was approximately 6.4 cm (2.5 inches) long by 2.54 cm (1 inch) in diameter. Heating was supplied by Nichrome resistance wire controlled by a voltage regulator. The purpose of the oven was to heat the gage section of the neat resin tensile specimens while leaving the gripping ears of the specimen, external to the oven, cool enough to prevent slipping and premature fracture in the Instron tensile jaws. In addition, the mounting of the specimens in the cool grips was much easier, thus limiting the loss of delicate specimens during installation. Trial runs showed an extremely small temperature variation about the set point, as measured by a thermocouple permanently mounted in the oven at the center of the gage length. Figure 13 shows the oven mounted in the Instron.

All of the data collected in neat resin tensile testing of ITGA specimens are reported in tables VIII through XIV. It should be noted that, in discussions of these data, the highest value obtained under a given set of conditions is used, for the most part, as representative for comparisons with other materials and conditions. While this is perhaps unusual, the difficulties inherent in manufacturing "perfect" neat resin tensile specimens are extremely numerous. The major problem, once a molding technique has been developed, is the occurrence of defects and the material sensitivity to these

defects in the specimen gage length caused by such things as monomer impurities, unreacted material, air borne debris, die surface defects, microscopic voids, scratches on the surface or sides, and machining surface finish or radius irregularities. All of these defects contribute to the reduction of observed strength and none act to increase strength. For this reason, it is felt that the use of high values is an acceptable technique for comparison purposes.

Table VIII gives baseline data on PMR-15 and three different FMW's of PMR-II; moldings (n = 1.67) were also tested before and after a 16 hour postcure at 316°C (600°F). A number of statements follow from an examination of the data:

a) In general, the strength, modulus and elongation are high for a cross-linked polyimide system of this type.

b) There appears to be no difference between molding cycles A and B.

c) Postcure increases both strength and strain-to-failure but does not affect modulus.

d) Tests on duplicate n = 1.67 moldings show no significant strength difference.

e) All of the materials appear to have roughly the same room temperature tensile strength with the exception of the 2.50 PMR-II which is slightly lower. Data discussed below indicate that the low values are a characteristic of this specific molding.

Table IX displays the tensile strength values of baseline specimens tested at 232°C (450°F). Again, all of the postcured materials appear to be in the same family except the 2.50 PMR-II. The non-postcured molding does not exhibit as high a strength as the postcured material. Again, no difference appears between cycles A and B.

Tables X through XIII give the room temperature tensile strength properties of the three FMW's after exposure to 316°C (600°F) for 209 hours, 382

hours, 572 hours and 1000 hours. As a convenience for comparison, in each of these tables, baseline values are shown for these materials before exposure. The retention of strength, elongation and modulus characteristics is quite high considering treatment conditions and the accompanying weight losses shown in ITGA weight loss curves. Note that the strength values of the n = 2.50 system show an increase. This seems to reflect the difference between the two n = 2.50 moldings tested. The 881-42 molding apparently had better tensile properties than the 881-44 molding.

Table XIV lists all the the 232°C (450°F) tensile test data collected on the neat resin moldings exposed to the ITGA conditions. The data reflect the same retention of original strength as shown with the room temperature tests.

The room and elevated temperature strength data given in tables VIII through XIV are displayed graphically in the bar charts shown in figures 14 and 15. This visual presentation of the data emphasizes: a) the equivelent tensile strength performance of the three PMR-II neat resin systems and b) the exceptional retention of strength characteristics, compared to unexposed specimens, after conditioning at 316°C (600°F) for 1000 hours.

On the basis of the data described above, two formulated molecular weight PMR-II systems were selected for subsequent investigation in composite form. The two systems chosen had n values of 1.67 and 2.50. The decision was based primarily on the isothermal performance of these two materials over the n = 1.30.

3.2.2 Moisture Exposure Testing

Little work has been done with polyimide resins in determining the moisture absorption characteristics and the effects on properties, especially in the neat resin form. Browning[12] has published an extensive study of a particular neat epoxy system in which he examined mechanisms and phenomena, but data of this kind are not readily available for polyimides. The following paragraphs describe the work performed on this program with the PMR-II (n = 1.67) material.

Machined neat resin tensile specimens, of the type described above, of PMR-II (n = 1.67) in both the postcured and non-postcured conditions were exposed to 97% relative humidity at 65°C (150°F) for 192 hours (eight days). The specimens were oven dried for 16 hours at 121°C (250°F) prior to test, mounted in acrylic racks and installed in the humidity chamber (Blue M Humidity Chamber, Model CPR-7702C). Weights were collected at incremental times by blotting the specimens of moisture and then weighing. At the conclusion of the humidity exposure, specimens were sealed in metal foil pouches and transported to the mechanical test area for test on the same day as removal from the humidity chamber.

Figure 16 displays the weight gain curves for the two material conditions tested. The average of triplicate determinations was used to plot the curves shown. It is interesting to note the high slope of the curve during the first 24 hours; the bulk of the moisture pickup occurred during this first time period. While the final values are not widely separated for the two different conditions, it was not anticipated that the postcured specimens would pick up more moisture than the non-postcured. The postcured specimens also displayed a slightly larger percent of dimensional growth with himidity exposure. Table XV lists the changes measured in both thickness and width. As can be seen the values are small, but the postcured specimens did show greater expansion. The behavior of the postcured vs. non-postcured neat resins in humidity is not understood, and the absolute values obtained are difficult to compare to other polyimide systems since little work has been reported on humidity testing, under the same conditions described above, on a spectrum of neat resin polyimide materials. However, it is possible that oxidation resulting from high temperature air postcure could provide more active sights for moisture pickup, which is in agreement with the dimensional changes observed.

The tensile test results, after humidity exposures, are shown in table XVI and in bar chart form in figures 14 and 15. Baseline data are shown before humidity exposure, and comparisons are made on the highest single strength value in a group. As can be seen, the loss in room temperature values on the postcured materials was not significant. The non-post-

cured material did, however, suffer considerable loss. At 232°C (450°F) the before and after values are equivalent for both conditions. The presumption is that the adsorped/absorbed moisture was driven off in reaching the 232°C tensile test temperature. The conclusion would be that, at least for the exposure conditions studied, the moisture pickup did not effect any permanent change in the polymer.

3.2.3 Glass Transition Temperature Determinations

Specimens of the three formulated molecular weight PMR-II neat resins (n = 1.30, 1.67, 2.50) were submitted to Polytechnic, Incorporated (Chicago, Illinois) for determination of glass transition temperature (Tg). In a preliminary trial, samples of the same molding were examined by both differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The TMA method yielded a more clearly defined transition point and was therefore chosen as the method used in subsequent analyses. Testing was done on a Perkin Elmer Model TMS-2 Thermomechanical System with a temperature rise rate of 10°C/minute under a nitrogen atmosphere and using an expansion probe weight of four grams.

The data collected on the three materials, including both postcured and non-postcured samples before and after humidity exposures are shown in table XVII. It is interesting to note that the postcured (16 hours at 316°C) specimens showed an increasing Tg with decreasing n value. A possible explanation of this behavior might be the increased cross-link density present in the lower n value systems. Other comparisons among the Tg data in table XVII indicate that the postcured moldings prepared with cycles A and B show no difference, while the non-postcured specimens show a 16°C (29°F) lower Tg for the cycle A material that only received one hour in the die at 316°C (600°F) as opposed to the cycle B cure which involved a three-hour hold at 316°C (600°F). Both of the humidity exposed specimens (postcured and non-postcured) gave values corresponding almost exactly with non-humidity treated specimens. This confirms behavior observed with elevated temperature tensile tests; i.e., the adsorbed/absorbed moisture was lost in getting to test temperature and no permanent changes were effected in the polymer by the humidity exposure.

3.2.4 Anaerobic Char Yield Determinations

Using neat resin moldings described above, char yield values were determined on PMR-15, a state-of-the-art epoxy system, three formulated weights of PMR-II and NR-059X. Triplicate samples approximately 25.4 x 25.4 x 1.5 mm (1 x 1 x 0.060 inch) were weighed and encased in small stainless steel foil (0.05 mm thick) envelopes. These were sealed by tightly folding the overlapping edges. To insure the exclusion of air, a total of three envelopes was used, one inside another. These envelopes were then placed in a laboratory muffle furnace and brought to 816°C (1500°F) over a 52 hour period by using a timer cam cycle and held for four hours at 816°C (1500°F).

The cam cycle was established using PMR-15 samples and a number of repetitive preliminary runs with trial and error adjustments of rise rate. All of the program samples were run at one time using this final cam cycle. Figure 17 displays the temperature curve obtained as determined with a thermocouple in the muffle chamber.

The three different PMR-II systems included n = 1.30, 1.67 and 2.50. All polyimide samples were postcured for 16 hours at 316°C (600°F) prior to pyrolysis. The state-of-the-art epoxy resin was made up of 50 parts by weight of Dow DER-331 liquid epoxy, 50 parts by weight of Dow DEN-438 epoxy-novolac and 20 parts of Uniroyal Tonox 60/40. The Tonox material is a liquid aromatic amine eutectic that contains approximately 60% of methylene dianiline with some higher functionality polymethylene polyanilines and 40% meta-phenylene diamine. The epoxy material was cast, cured at 149°C (300°F) and postcured at this temperature for 16 hours.

Table XVIII lists the average char yields observed with each of the materials. Quite clearly, the PMR-15 yields the highest char value, with the epoxy system showing the lowest value. All of the PMR-II systems were closely grouped, with the NR-059X exhibiting a slightly higher char retention value.

Aside from the quantitative char yield value, a second important characteristic is the quality or integrity of the remaining char. The PMR-15 samples exhibited the greatest appearance of integrity. These samples were sound, emitting a ringing noise when dropped on a hard surface; retained sharp edges; and showed no blistering. The epoxy samples did not show any obvious blistering and were covered with a layer of coherent soot. The three PMR-II materials and the NR-059X were similar to one another in appearance. The surfaces were smooth and shiny, but all samples expanded through the thickness, displaying a blistered effect. A microscopic examination of polished cross-sections confirmed the superior appearance of the PMR-15. All of the materials, except the PMR-15, displayed large, extensive voids. The PMR-15 exhibited some very fine porosity, mostly along one face of the specimen.

4.0 COMPOSITE PROCESSING

As was noted above, two formulations of the PMR-II system were chosen for further evaluation in composite form. These had n values of 1.67 and 2.50. This choice was based primarily on the superior thermo-oxidative stability shown by these resins in ITGA tests of neat resin moldings. Additionally, the NR-059X fully formulated PMR-II precursor from DuPont was examined in composite form. The paragraphs below describe the evaluations conducted.

4.1 Freshly Prepared PMR-II

Using freshly prepared monomer solutions, with n values of 1.67 and 2.50, composites were fabricated with C-3000 cloth, a limited evaluation performed, and the decision made to de-emphasize the 2.50 material. Additionally, unidirectional composites were prepared with Fortafil-3 fiber.

4.1.1 Celion C-3000 Cloth Composites

Using the techniques described in Section 2.1.1, 50 w/o monomer solutions were prepared, spread onto pre-weighed sections of the C-3000 cloth, and the prepreg staged at room temperature to reduce the volatile content to approximately 11%. Using this prepreg, a series of 10.2 x 10.2 cm (4 x 4 inches) and 21.6 x 21.6 cm (8.5 x 8.5 inches) laminates were die molded of each n value for comparison of fabrication response. The laminates were seven plies thick (molded thickness of 2.3 mm) and were molded by using an oven imidize for one hour at 204°C (400°F), a die insertion temperature of 232°C (450°F) with a 10 minute hold, and rise to 316°C (600°F) of 20 minutes with pressures of 3.4 and 6.9 MPa (500 and 1000 psi).

Two of each of the 21.6 cm x 21.6 cm laminates of the 1.67 and 2.50 PMR-II laminates were sectioned, and half subjected to a 16 hour postcure at 316°C (600°F). All of these panels were submitted for sonic inspection prior to machining into mechanical test specimens.

In molding the n = 2.50 composites in a 10.2 x 10.2 cm die, it was observed that zero resin expulsion was experienced at both 3.4 and 6.9 MPa (500 and 1000 psi) pressures. The 1.67 composites exhibited adequate flow at 3.4 MPa. For this reason, the larger 21.6 x 21.6 cm moldings were prepared using the higher pressure for the 2.50 system and 3.4 MPa for the 1.67 composites. Despite this, the flow of the 2.50 material was so limited as to yield composites exhibiting noticeable void contents. This was demonstrated in the ultrasonic C-scans of these laminates. Figures 18 and 19 display representative samples of C-scans from the C-3000 composites with the 1.67 and 2.50 matrices. The dark area, which indicates defect areas, can be seen to be of significant size with the 2.50 system.

The mechanical property values collected on these laminates are shown in tables XIX and XX. A review of the data indicates two trends of significance: a) the 1.67 system displays superior, short-term high temperature properties and b) the 1.67 material shows a beneficial response to postcure for 16 hours at 316°C (600°F). It should be noted that the properties shown compare well with those reported by Celanese on the C-3000 fabric (table XXI).

In reviewing glass transition temperature data reported, the Tg of the 1.67 neat resin was determined to be about 10°C higher than the 2.50 material, and the neat resin mechanical properties were in an equivalent range. While the isothermal gravimetric data (mean values) at 316°C (600°F) for the two n values showed the expected superiority of the 2.50 material, the best individual values for the 1.67 system approach those of the 2.50 values.

Thus, on balance, comparing fabricability, short term composite property levels and long term isothermal behavior, it was concluded that the 1.67 level of the PMR-II system would be the preferred formulated molecular weight system to emphasize in the following portion of the program.

4.1.2 Fortafil-3 Composites

Using the PMR-II with an n value of 1.67, prepreg was prepared from the 40,000 filament F-3 tow with a methyl alcohol solution by winding onto

a 1.52 m (5 feet) diameter drum. A molded ply thickness of 0.25 mm (10 mils) was targeted. Details of this prepregging procedure will not be given since the process is described elsewhere[2].

Nine ply laminates of 10.2 x 10.2 cm (4 x 4 inches) and 21.6 x 21.6 cm (8.5 x 8.5 inches) were molded. Prepreg stacks were imidized for one hour in an air circulating oven at 204°C (400°F), inserted in a preheated die at 232°C (450°F), held under contact pressure for 10 minutes, and brought to 316°C (600°F) over a 20 minute period. Pressures of 3.4 MPa and 6.9 MPa (500 psi and 1000 psi) were used.

No visual flow was observed at 3.4 MPa (500 psi). This is felt to be a function of fiber reinforcement surface characteristics, perhaps a reflection of the non-sized fiber, since the C-3000 laminates with the 1.67 matrix displayed adequate flow at this molding pressure.

Panels molded at both 6.9 and 3.4 MPa (1000 and 500 psi) were submitted for sonic inspection. The sonic results showed significant void contents in panels molded at 3.4 MPa. The panels molded at the higher pressure displayed approximately 1% void area in concentrated areas associated only with panel edges. These results were confirmed with photomicrographs.

Flexural and short beam shear values were determined on the Fortafil 3 reinforced PMR-II (n = 1.67) composites molded at the higher pressures. Table XXII lists data collected on both postcured and non-postcured material. These can be compared to vendor reported properties in an epoxy matrix (table XXIII). As can be seen, the values are quite high, showing good retention at 316°C (600°F). On the basis of these data, it was concluded that the solvent prepregging technique and the standard molding cycle at 6.9 MPa (1000 psi) represented appropriate methods and these procedures were carried forward into subsequent phases of the program.

4.2 NR-059X Composites

Using the same techniques as for the freshly prepared monomer solutions, Celion C-3000 cloth prepreg was prepared with du Pont NR-059X, an experimental,

fully formulated PMR-II (n = 1.67) precursor, and 21.6 x 21.6 cm (8.5 x 8.5 inch) laminates fabricated with a standard PMR-II die molding cycle using 3.4 MPa (500 psi). A visual inspection of these laminates indicated that the corners of the laminates did not seem to be completely filled due to lack of resin flow. These observations were confirmed by examining the ultrasonic C-scans of these laminates. The defect areas can be seen in the corners of the C-scans shown in figures 20 and 21.

The NR-059X precursor solution was stored at -18°C (0°F) and withdrawn each week for the preparation of a new prepreg; this was continued for a period of five weeks. Each week a 10.2 x 20.4 cm (4 x 8 inch) laminate was fabricated using the same standard die molding cycle, postcured for 16 hours at 316°C (600°F) and submitted for ultrasonic inspection. Figures 22 through 26 show this series of C-scans. After two weeks of storage, an increase in the defect area can be observed; this level was maintained for the next three weeks after which testing was discontinued.

For comparison with the C-scans discussed above, figure 27 shows the C-scan of a C-3000 laminate prepared with fresh PMR-II (n = 1.67) solution using identical molding and inspection techniques. As can be seen the laminate appears essentially void free.

Tables XXIV and XXV give mechanical test property data collected on C-3000/NR-059X laminates. Test specimens were taken from sections of the laminates determined to be void free by sonic inspection. Table XXIV lists values for a non-postcured laminate that was cured for one hour at 316°C (600°F) in the tool. Note the low values obtained in 316°C (600°F) test and the evidence of blistering observed after test exposure to 316°C (600°F). This sluggish response in cure was previously noted in molding neat resin samples.

Short beam shear and flexural strength values for postcured laminates are listed in table XXV. Shown are data from laminates prepared with the NR-059X solution as-received and after five weeks storage at -18°C (0°F). While the five week material at 316°C (600°F) was lower than the as-received

solution, these values, in general, compared to freshly prepared laminate values. Specimens were taken from sound areas of the laminates as indicated by ultrasonic C-scan; the conclusion was that the polymer formed in the composite by the NR-059X after five weeks storage did not seem to have deteriorated.

Summarizing work performed with both neat resins and composites of the NR-059X, it was concluded that at this time certain processing behavior inhibits unqualified acceptance of the material as presently formulated. In neat resin molding, it was found that the material responded differently from the freshly prepared PMR-II, requiring different process cycles to obtain sound moldings. The neat resin seemed to react more slowly and evolved gases over a longer interval during molding. Additionally, postcure of the neat resins showed high weight losses even after three hours in the tool at 316°C (600°F). With carbon cloth reinforced composites, the NR-059X prepregged without difficulty but yielded die molded laminates of lesser quality (based on sonic defect area) than with freshly prepared PMR-II with the same n value and identical molding cycles, as a result of a limited flow capability shown by the NR-059X system. It is perhaps possible that formulation modifications and/or more intensive fabrication studies, including autoclave molding trials, might yield a more easily processed material. However, at the present level of development, it was not felt that the convenience of the fully formulated system justifies the increased process difficulties encountered. For this reason, further work with the NR-059X on the program was limited.

5.0 COMPOSITE CHARACTERIZATION

The characterization of composites with PMR matrices was conducted with both C-3000 and F-3 reinforcements. Evaluations included isothermal gravimetric analysis (ITGA) testing, with both weight loss and property change with time exposure; changes in weight and properties with moisture pickup; and the development of a laboratory method for determining the fiber release behavior of composites during incineration, with a comparison of three different matrix systems. Details of each of these studies are given below.

5.1 Isothermal Gravimetric Analysis

Using the techniques described above, PMR-II (n = 1.67) laminates were prepared with both F-3 tow and C-3000 cloth reinforcements. Acceptance techniques included ultrasonic inspection, resin content determination by acid digestion, and selected microscopy. Additionally, previously prepared laminates of NR-059X and PMR-II (n = 2.50), along with newly fabricated PMR-15 composites, all with C-3000 cloth, were subjected to the ITGA portion of the evaluation (weight change only).

Placques of all of these materials were subjected to 1500 hours at 316°C (600°F) using the same ITGA technique described for fiber and neat resin studies (Cf. Sections 2.2.2 and 3.2.1). The placques were approximately 3.8 x 20.3 cm (1.5 x 8 inches), except for the PMR-15 laminates which were 10.2 x 2.5 cm (1 x 4 inches). These placques were held in a vertical position and separated from one another in the ITGA chamber by the use of stainless steel wire racks. Figure 28 shows the placques installed in the ITGA chamber.

Weight changes and mechanical property determinations were made at 300, 600, 1000 and 1500 hours. Baseline composite flexure and short beam shear data, before ITGA exposure, are shown in tables XXVI and XXVII. The values appear to be consistent among themselves with regard to multiple laminates and are representative of the maximums available from the reinforcements. The shear values for the F-3 laminates are lower than usually obtained with other industry fibers in the modulus range of 30 million psi, but agree with

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those published by the vendor (see table XXIII). The values in tables XXVI and XXVII form the basis for comparison on the C-3000 and F-3 PMR-II laminates used in both the ITGA evaluations and the humidity exposure testing discussed in a subsequent section.

Figure 29 shows the curves of composite weight loss against time at 316°C (600°F); also shown is a curve for PMR-15/HM-S from a previous program[4]. A number of interesting comparisons of isothermal performance can be made among the material combinations evaluated. First it is clear that the two best PMR-II systems (1.67/F-3 and 2.50/C-3) are superior to either of the PMR-15 combinations shown. The material showing the least weight loss (1.67/F-3) possessed two advantages over other PMR-II systems examined: a) the isothermally stable F-3 fiber and b) its unidirectional orientation, as opposed to the bi-directional cloth reinforcement. The contribution of the fiber to isothermal performance of the composite was discussed in section 2.2.1 and can also be seen in the difference between the two PMR-15 curves. The F-3 was shown to be more stable than the C-3000 in bare fiber ITGA (figure 6). With regard to use of a bi-directional cloth reinforcement, the high number of fiber ends exposed in a cloth composite would seem to indicate that a potentially higher weight loss might be experienced presuming a relatively oxidation sensitive fiber. It is felt that the disparity displayed between the 1.67 matrix with the F-3 and the C-3000 reinforcement perhaps reflects both of these factors.

The better performance shown by the NR-059X composites with the C-3000 over the 1.67 freshly prepared monomer system with the same reinforcement is puzzling since the NR-059X is reported as having the same 1.67 formulated molecular weight (FMW). The effect of formulated molecular weight can be seen in the comparison of the 2.50 and 1.67 composites with C-3000. The neat resin ITGA (figure 9) displays the superior weight retention of the 2.50 system but not nearly by so wide a margin. Perhaps a fiber/resin interaction exists which is more responsive to the composition of the lower FMW matrix.

At the conclusion of each of the exposure intervals, placques were machined into triplicate flexure and short beam shear specimens and tested at 316°C (600°F). While specimens exposed for 1500 hours at 316°C (600°F) did show the effect of loss of resin on the surface, they did not exhibit the appearance of having loose, detached fibers as they were removed from the ITGA chamber. During machining, of course, it was clear that significant amounts of matrix had been lost and fibers were loosened. These conditions are difficult to depict; however, figures 30 and 31 are presented to display the lack of loose surface fibers after the 1500 ITGA treatment.

The results of the mechanical testing of the ITGA specimens are shown in tables XXVIII and XXIX. These data, shown as percent of strength retention, are plotted in figures 32 and 33. For comparison, in each figure, data from a previous program[1] on PMR-15/HM-S are also plotted. In considering the PMR-II composites, the superior performance of the F-3 reinforced laminates, compared to the C-3000 cloth laminates, can perhaps be explained on the basis of the unidirectional fiber orientation and the better isothermal resistance of the bare F-3 fiber.

When comparing the PMR-II curves with the PMR-15/HM-S, it must be remembered that both the fiber and the resin are different, making it difficult to explain the mixed performance. It could perhaps be reasoned that, during different portions of the ITGA cycle, the isothermal performance of the fiber and resin elements vary in the importance of their contribution to the composite behavior. For example, during the first portion of the cycle, the resin may be a dominant factor, while later, both elements play a role.

In comparing the trends of shear and flexure strength retention displayed by the curves, it is important to note different characteristics are required from the composite during these tests. While the flexure test introduces a shear component, a large measure of the load is carried in tensile and compression, while the short beam shear performance is highly dependent on the fiber/resin interface. In discussing these data, it should also be noted that some inconsistencies exist when compared to other

work reported[3][13] on PMR-II composites. The referenced data show generally higher property retention with time and a correlation between shear and flexure behavior. This work was, of course, performed in different laboratories and with different fiber batches, so the apparent inconsistencies are difficult to assess.

In summary, it is difficult to draw specific conclusions regarding individual material performance, but it is clear that the thermo-oxidative process is complex and that an interaction between matrix and fiber (both composition and orientation) exists. All of these elements must be considered in selecting a system for use in severe thermal environments.

5.2 Composite Moisture Exposure Testing

Using techniques described for neat resin exposures (see section 3.2.2), two composite systems were subjected to 97% relative humidity at 65°C (150°F) for 192 hours (8 days). The two materials were PMR-II (n value of 1.67) with both F-3 tow and C-3000 cloth reinforcements. Both flexure and short beam shear specimens (for triplicate determinations) were machined to size prior to insertion in the humidity chamber. All specimens were oven dried for 16 hours at 121°C (250°F) before humidity exposure. Weight and dimensional changes were recorded and mechanical properties determined after exposures.

Figure 34 shows a plot of moisture weight gain against time of exposure. The higher weight gain and the more rapid rise to that level exhibited by the C-3000 composites is felt to reflect the existence of more paths for absorption along the fiber/resin interface available in the bi-directionally reinforced cloth specimens. The absolute level of weight gain is generally consistent with the data shown in figure 16 on the neat resin, when calculations are made to allow for the fiber content of the composites. Thickness change values were inconsistent and showed no clear trend. Final width measurements indicated a slight gain in the F-3 composites (+0.2%) and no change in the C-3000 composites due to the restraining influence of the 90 degree fibers in the cloth.

Table XXX displays all of the mechanical property data collected on both materials. As can be seen, the room temperature values were not changed in any significant amount, with all showing minor losses with the exception of the F-3 laminate which showed a small (8%) increase in flexure strength. While this was not expected, C. B. Delano, et al[14] report having reviewed literature on polyimides in moist environments that indicated a divergence of property performance ranging from ". . . strength increases to significant degradation."

The elevated temperature testing of the humidity exposed composites showed a decrease in mechanical properties. The short beam shear strengths show an approximate 34% decrease for both materials. The flexure strength of the F-3 composites dropped 19%, while the C-3000 flexure strength decreased only 8%. This loss of properties at elevated temperature after humidity exposure was not exhibited by the neat resin testing discussed earlier. It seems possible that moisture is not lost in heatup to test temperature as rapidly from a composite as from a neat resin molding or, alternately, that the moisture affects the fiber resin interface providing a retarded release of the absorbed moisture.

5.3 Composite Fire Testing

Recently, considerable concern has been exhibited with regard to release of graphite fiber fragments during the accidental or deliberate incineration of graphite fiber reinforced composites. It has been shown that fiber fragments can be carried long distances by wind currents and have, on occasion, caused electrical and electronic apparatus failure by arcing and shorting of contacts. The ability of a resin matrix in constraining fiber release during incineration is becoming an important criterion in the selection of composite systems for hardware applications. For this reason, it was appropriate to evaluate, on a cursory basis, the incineration and fiber release characteristics of certain PMR composites and compare them with some known baseline. To this purpose, a test apparatus was developed and three composite systems were evaluated. The details of these investigations are described below.

5.3.1 Fire Testing Apparatus Development

Identification of the mechanisms contributing to the retention of reinforcing fibers during the burning of a composite is obviously a complex task and is dependent on exposure conditions and component geometry, as well as the basic material characteristics. Equally as difficult is designing a laboratory method that simulates anticipated field conditions and yields data of significant value. It was felt that a reasonable goal for a screening test would combine a heat source with a shock or a gas velocity mechanism that would provide information about material loss, debris characteristics and establish a rough ranking for resin/matrix combinations.

With these criteria in mind, a burner test rig was evolved through a series of trials with different material families under various test conditions. The basic unit finally selected consisted of a radiant heat source, a device to administer a burst of air to provide a shock to the specimen, and a filter to trap released debris. Figure 35 displays a schematic of the test rig. Figure 36 is a close-up view showing several of the important features.

The specimen, 2.5 x 7.6 cm (1 x 3 inches), was mounted in a holding fixture at 45 degrees to the horizontal. The burner was normal to the specimen face and 2.54 cm (1 inch) from it. The radiant burner (Model K-201, Selas Corporation, Dresher, Pennsylvania) was fired with natural gas and air after passing through a venturi mixer (Pyronics, Inc., Cleveland, Ohio). Flow meters were used in the gas lines upstream of the mixer. Flow rates were: air, 957 l/hr (33.8 ft^3/hr); natural gas, 102 l/hr (3.6 ft^3/hr), which approaches a stoichiometric mixture. Optical pyrometer readings of the ceramic bowl of the burner indicate a maximum surface temperature of 1082°C (1980°F). The specimen was exposed for 10 minutes, cooled in place and withdrawn for weighing. After weighing the specimen was replaced, burner-exposed side down, and three air shocks administered to this face, forcing any loose fibers from the specimen up the exhaust stack to the glass cloth scrim filter. The air shocks were delivered by activating a solenoid

valve which suddenly released 19.77 cc (1.2 in^3) of air at 621 KPa (90 psi) through a 9.5 mm (3/8 inch) diameter tubing near the face of the specimen. The specimens were then reweighed and the filter withdrawn for examination of the debris.

5.3.2 Composite Fire Testing

Composites with three different matrices were evaluated; PMR-15, PMR-II with an n value of 1.67, and the same epoxy-novolac system described in the neat resin anaerobic char testing (see section 3.2.4). All of these matrices were combined with the C-3000 cloth reinforcement into composites with a nominal fiber volume of 60 v/o. All panels were inspected ultrasonically and found to be essentially void free.

Table XXXI presents specimen weight loss data after both thermal exposure and air shock on these three materials. As can be seen from the data, the PMR-15 composite system experienced the lowest loss in both thermal exposure and after air-shock. The PMR-II (n = 1.67) composites lost significantly more material by both criteria, and the epoxy-novolac system showed the greatest loss by a very wide margin. Note that individual specimen groups gave reproducible results from repeated tests. In order to confirm reproducibility in day-to-day operations, a second set of specimens from the same PMR-15 laminate was run some days later than the first tests. The weight loss figures coincide quite closely with the first run, indicating that test conditions were reproducible with the gages and flow meters employed.

Figure 37 shows typical specimens of each of the materials evaluated after fire test. Figures 38 through 40 are photographs of typical fiber debris collected on the exhaust stack screen from each of the three materials. It can clearly be seen that the quantity of debris collected from each material corresponds with the weight loss measurements for these materials given in table XXXI.

Figure 41 is a series of bar charts comparing neat resin matrix pyrolysis loss data from anaerobic char tests described in section 3.2.4,

composite specimen loss in thermal exposure and after air-shock. It is apparent that, within the limits of the matrices, fiber type and orientation studied, there is a direct relation between matrix char yield and fiber retention characteristics.

The conclusion that a direct relation exists between char content and fiber retention was based on limited testing and should be qualified. In examining the fiberous debris trapped in the filter from the specimens described, it was clear that the bulk of the debris represented fill yarns from the cloth reinforcement. As the matrix was thermally consumed, the one inch long fill yarns (perpendicular to the long axis of the specimen) were free to be dislodged by the air jet. It was noted that a number of unidirectional materials tested during equipment trials released significantly fewer fibers. The continuous axial fibers in this latter case were anchored in the non-exposed, cool portion of the specimen and were not easily dislodged by the air shocks.

It is obvious that the test method is specimen geometry dependent, and using a larger area specimen with the same limited thermal exposure area would produce improved fiber retention. It was also noted under microscopic examination that the individual fibers captured on the filter were essentially void of any resin char and the fiber bundle fragments had extremely small amounts of char debris holding them together. This would indicate that a sufficiently oxidizing environment existed during exposure to essentially consume the carbonaceous resin char but not the more oxidation resistant reinforcement. In other preliminary tests, epoxy specimens, with high strength graphite fibers (a less oxidation resistant type of reinforcement), continued to glow for some time after removal of the heat source, indicating graphite fibers were being oxidized. In this case, weight loss after burner exposure would be high, but the amount of collected debris would be less since many of the individual fibers would be totally consumed.

In summary, both fiber type and orientation are important and must be considered strong contributors to the performance of candidate composite systems in the test approach described. Considerable test history would have to be collected with multiple resins, fibers and orientations before universally applicable conclusions could be drawn from this type of testing. However, despite the shortcomings described, it is felt that the test method described represents a useful and inexpensive tool for the rough screening of fiber release performance. It is concluded that the char/fiber release correlation is real, and that the ranking of the three materials would reflect performance in an actual combustion environment.

6.0 PROGRAM CONCLUSIONS

Specific conclusions on such things as processing details and material properties are given in the body of the text. The conclusions presented below represent more general statements that summarize the major findings of the program.

1. The second generation PMR matrix system (PMR-II) was found to provide the same ease of processing of PMR-15. PMR-II composites also yielded the excellent mechanical properties typical of those from PMR-15. The preferred intermediate formulated molecular weight PMR-II matrix, coupled with a relatively stable fiber, provided composites with superior weight and flexure strength retention in isothermal evaluation when compared to PMR-15 laminates studied on a previous program. Shear strengths of the PMR-II composites were, however, affected more rapidly in the isothermal testing than the previously studied PMR-15 system.

2. Three formulated molecular weight levels of the PMR-II matrix system were evaluated and found to exhibit both flow and thermo-oxidative stability characteristics which were related to formulated molecular weight. The highest molecular weight material showed the lowest flow in composite processing and the highest weight retention in neat resin isothermal gravimetric testing.

3. An experimental fully formulated PMR-II precursor solution was purchased and subjected to a limited evaluation. No difficulty was experienced with prepregging, and both mechanical properties and isothermal performance were acceptable. However, inadequate flow was observed in composite processing and a limited storage capability was exhibited. These latter characteristics inhibit complete acceptance of this first iteration system in its present state of development.

4. The contribution of fiber composition and/or orientation in the thermo-oxidative stability of composites was demonstrated. This area of investigation deserves further, more intensive examination in terms of

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specific property effects; fiber orientation and matrix contributions; and mechanisms.

5. Humidity testing of both neat resin and composite PMR-II samples revealed significant weight pickup in 192 hour exposures at 65°C (150°F) and 97% relative humidity. In tensile testing, humidity exposed specimens of postcured neat resin and composites showed no significant strength loss at room temperature. Tensile strength values at 232°C (450°F) of the neat resin were not affected, but the composite material samples did exhibit some loss in properties at elevated temperature.

6. An inexpensive fire test burner rig for the determination of graphite fiber release characteristics was constructed and demonstrated to be quite adequate for the rough screening of composite material systems. It was established that a correlation exists between the anaerobic char yield of matrices and the fiber release performance of composites employing these matrices.

7.0 RECOMMENDATIONS FOR FURTHER WORK

A review of the efforts on this program has identified certain areas in which further work should be pursued to obtain a more complete understanding. These include:

1. Isothermal gravimetric testing with emphasis on the role of the matrix and the fiber composition and orientation in influencing composite performance. Studies should include an examination of a number of various materials, test method parameters and the investigation of fiber/resin interface changes.

2. Humidity testing of a range of polyimide matrices to achieve a better understanding of the effects and mechanisms, and a comparison of the various polyimide families in a standardized test procedure.

3. Fire and char testing to more completely define the relation of anaerobic char content of the matrix and fiber release characteristics on a full range of structural matrices and reinforcements.

4. The goal of a fully formulated PMR-II precursor solution is a desirable one, and while the first development material was not completely satisfactory, it seems possible that further work in this area might produce a useful system for commercial application.

TABLE I

STOICHIOMETRY OF VARIOUS FORMULATED
MOLECULAR WEIGHT PMR-II RESINS

Moles of HFDE, n[a]	Formulated Molecular Weight[b]
1.30[c]	1071
1.67[c]	1262
2.00	1432
2.50[c]	1690

Note: (a) Molar ratio HFDE/PPDA/NE equals n/(n+1)/2

(b) $FMW = (n)MW_{HFDE} + (n+1)MW_{PPDA} + 2\ MW_{NE} - 2(n+1)(MW_{H_2O} + MW_{CH_3OH})$
where MW represents the molecular weight of the compound indicated by the subscript.

(c) Denotes the systems studied in this program.

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TABLE II (REF. 9)

SUMMARY OF 316°C (600°F) ISOTHERMAL AGING DATA OF GRAPHITE YARN

Manufacturer	Graphite Type	Weight Loss by Percent					
		Hours:					
		73	233	281	401	473	593
Celanese	Celion 3000 [1] Package 41	1.24	3.03	3.73	5.79	7.58	10.22
Celanese	Celion 3000 [1] Package 208 (U.S.P.)	1.16	2.71	3.25	5.12	6.65	9.13
Hercules	HTS-2	3.78	10.57	12.66	18.22	21.44	25.79
Union Carbide	T-300 (H.P.) [2]	2.42	7.68	10.49	19.50	24.91	32.32
Morganite	Modmor II	0.22	0.36	0.40	0.42	0.49	0.52

[1] Contains a coating of NR150A2 polyimide resin approximately 2% by weight

[2] Contains a high temperature epoxy sizing approximately 1.5% by weight

TABLE III

RANKING OF CARBON FIBERS
ACCORDING TO PERCENT WEIGHT LOSS[1]
AFTER 700 HOURS IN AIR AT 600°F (316°C) (REF. 8)

Carbon Fiber	Lot No.	% Weight Loss
"Fortafil"[3] 5	R128(B)C	0
"Magnamite" HMS	34-1	0.08
"Modmor" II-S	C266/12	0.08
"Fortafil"[3] 3	RS494(B)B	0.18
"Modmor" II-S	265-2	0.38
"Magnamite" HTS - New	66-7	1.2
"Celion"[2] - Epoxy Sized	6711	3.5
"Celion"[2] - Unsized	6Y11	5.5
"Magnamite" HTS - New	66-7	15
"Magnamite" HTS - New	66-7	16
"Magnamite" HTS - Old	54-4	49
"Magnamite" AS	36-3	67
"Fortafil"[3] 3U	2-1093 W/8C	97

Notes: (1) Two-hour reading subtracted from total

(2) 6000 fiber tow.

(3) 40,000 fiber tow.

TABLE IV

WEIGHT LOSS OF VARIOUS GRAPHITE FIBERS AFTER THREE HOURS AT 773°C (1423°F) IN AIR (REF. 10)

Fiber	% Carbon	Modulus GN/m^2	Percent Weight Loss
High Modulus Celion Variant	99.7	413	0.05
GY-70	99.3	517	0.1
High Modulus Celion Variant	99.6	345	0.2
UCC VS A11 Pitch Based Fiber	--	345	0.6
VM-0032 (UCC Non-Woven Mat)	--	220	0.7
HMS (Batch 42-2)	--	345	3.3
Celion 3000/6000	93.0	241	3-5
UCC Pitch Based (Continuous Roving)	98.0	172	4.6
Thornel 50	--	345	9.6
Great Lakes 4T	--	276	9.9
HTS	--	276	5-30
Modmor III	94.8	241	98.3
Hercules AS	93.9	241	98.7
Panex 30A	--	207	98.8
Thornel 300	91.3	241	99.3

TABLE V

TYPICAL FORTAFIL 3 FIBER PROPERTIES
REPORTED BY THE VENDOR

TYPICAL FIBER OR TOW PROPERTIES (SINGLE FILAMENT TESTS)

Tensile Strength (KSI on 1 " Gage Length)	360
Tensile Modulus (MSI)	30
Density (gm/cc)	1.71
(lbs/in3)	0.0617
Tow Cross-Sectional Area (in2)	0.0033
Tow Yield (ft/lb.)	395
Electrical Conductivity (ohm-1cm-1)	570
Specific Heat (cal/gm/°C)	0.22
Axial Coefficient of Thermal Expansion (10-6/°C)	0.11
Axial Thermal Conductivity (W/cm°C)	0.20
Oxidative Resistance (%Wt. loss after 700 hrs. at 316 °C)	0.18
Surface Area (M2/gm)	1.0
Chemical Analysis - Carbon (%)	96.5
Nitrogen (%)	2.8
Oxygen (%)	0.1
Hydrogen (%)	0.3
Ash (%)	0.3

TABLE VI

TYPICAL CELION 3000 FIBER PROPERTIES REPORTED BY THE VENDOR

	U.S.		International	
Fiber Properties	**Typical**	**Minimum**	**Typical**	**Minimum**
Tensile Strength*	400×10^3 psi	360×10^3 psi	2758MPa	2482MPa
Tensile Modulus*	34×10^6 psi	33×10^6 psi	234GPa	227GPa
Ultimate Elongation*	1.2%	1.1%	1.2%	1.1%
Density	0.064 lb/in^3	0.062 lb/in^3	1.76 g/cm^3	1.72 g/cm^3
Electrical Resistivity	9000 Ω-mil-ft		1500μ Ω -cm	
Yarn/Tow Characteristics				
Filament Diameter	0.28×10^{-3} in		7.1×10^{-6} m	
Filament Shape	Round		Round	
Filament Count	3000		3000	
Fiber Area in yarn cross section	1.8×10^{-4} in^2		.12 mm^2	
Yield	2410 yd/lb	2343 yd/lb	0.206 g/m	0.189 g/m
Twist HTA-7W	0.4 turns/in		15 turns/m	
HTA-7	None		None	
Size Level	1.1%	0.8%	1.1%	0.8%
Splices	A maximum of 6 per 4 lb. (1.8 kg) package			

*Impregnated Strand Test Method

TABLE VII

WEIGHT GAIN OF GRAPHITE FIBERS IN AMBIENT AIR
FOR FIVE HOURS AFTER 1000 HOUR EXPOSURE AT 316°C (600°F)

	Fortafil 3 (%)	C-6000 (%)
Sample #1	0.8	9.1
Sample #2	0.8	8.5
Sample #3	0.7	8.5
Avg.	0.8	8.7

Notes: (-) Weight pickup was noted after fibers were removed from the 316°C (600°F) ITGA oven, cooled, weighed and thermal loss data recorded. Samples were reweighed after five hours in laboratory ambient conditions and weight gain noted.

(-) All samples returned to original weight after an additional exposure of one hour at 316°C (600°F).

TABLE VIII (S.I. UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES
OF PMR NEAT RESIN MOLDINGS

Material	Moles of HFDE, n	Mold Cycle	Postcured	Ult. Tensile Strength, MPa	Total Elongation, %	Mod. of Elasticity, GPa	Ident.
PMR-II	1.30	B	Yes	76.5	2.5	4.1	881-63
				81.4	2.5	4.1	
				67.6	1.7	5.5	
	1.67	A	Yes	59.3	1.7	4.1	881-29
				82.0	2.2		
				74.5	2.1		
		A	Yes	80.0	-	-	881-15
				74.5	-	-	
				45.5	-	-	
		B	Yes	77.2	2.5	4.1	881-46
				67.6	2.1		
				64.8	2.0		
		A	No	47.6	1.1	4.8	881-19
				51.7	1.3	4.1	
				49.6	1.1	4.8	
		B	No	45.5	1.2	4.1	881-48
				33.8	0.8		
				55.8	1.7		
	2.50	B	Yes	63.4	1.8	4.1	881-44
				63.4	1.7	4.1	
				66.2	2.3	3.4	
PMR-15	-	B	Yes	77.2	2.4	4.1	833.31
				84.8	2.5		
				81.4	2.7		

TABLE VIII (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES
OF PMR NEAT RESIN MOLDINGS

Material	Moles of HFDE, n	Mold Cycle	Postcured	Ult. Tensile Strength, ksi	Total Elongation, %	Mod. of Elasticity, msi	Ident.
PMR-II	1.30	B	Yes	11.1	2.5	0.6	881-63
				11.8	2.5	0.6	
				9.8	1.7	0.8	
	1.67	A	Yes	8.6	1.7	0.6	881-29
				11.9	2.2	0.6	
				10.8	2.1	0.6	
		A	Yes	11.6	-	-	881-15
				10.8	-	-	
				6.6	-	-	
		B	Yes	11.2	2.5	0.6	881-46
				9.8	2.1	0.6	
				9.4	2.0	0.6	
		A	No	6.9	1.1	0.7	881-19
				7.5	1.3	0.6	
				7.2	1.1	0.7	
		B	No	6.6	1.2	0.6	881-48
				4.9	0.8	0.6	
				8.1	1.7	0.6	
	2.50	B	Yes	9.2	1.8	0.6	881-44
				9.2	1.7	0.6	
				9.6	2.3	0.5	
PMR-15	-	B	Yes	11.2	2.4	0.6	833-31
				12.3	2.5	0.6	
				11.8	2.7	0.6	

TABLE IX (S.I. UNITS)

232°C TENSILE STRENGTH OF PMR NEAT RESIN MOLDINGS

Material	Moles of HFDE, n	Mold Cycle	Postcured	Ult. Tensile Strength, MPa	% of R.T.[(a)] Strength Retained	Ident.
PMR-II	1.30	B	Yes	49.6 41.4 30.3	61	881-63
	1.67	A	Yes	31.0 51.7 37.2	63	881-29
	1.67	B	Yes	33.8 46.9 49.6	64	881-46
	1.67	B	No	31.0 31.0 24.1	56	881-48
	2.50	B	Yes	35.9 38.6 35.2	58	881-44
PMR-15	-	B	Yes	55.2 58.6 50.3	69	833-31

(a) Based on single highest value in R.T. and 232°C test groups from same molding.

TABLE IX (U.S. CUSTOMARY UNITS)

450°F TENSILE STRENGTH OF PMR NEAT RESIN MOLDINGS

Material	Moles of HFDE, n	Mold Cycle	Postcured	Ult. Tensile Strength, ksi	% of R.T.[(a)] Strength Retained	Ident.
PMR-II	1.30	B	Yes	7.2 6.0 4.4	61	881-63
	1.67	A	Yes	4.5 7.5 5.4	63	881-29
	1.67	B	Yes	7.1 6.8 7.2	64	881-46
	1.67	B	No	4.5 4.5 3.5	56	881-48
	2.50	B	Yes	5.2 5.6 5.1	58	881-44
PMR-15	-	B	Yes	8.0 8.5 7.3	69	833-31

(a) Based on single highest value in R.T. and 450°F test groups from same molding.

TABLE X (S.I. UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 209 HOURS AT 316°C

Moles of HFDE, n	Ult. Tensile Strength, MPa	Total Elong., %	Mod. of Elasticity, GPa	Ident.
1.30				
Before Exposure[a]	81.4	2.5	4.1	881-63
After Exposure	81.4	2.7	4.1	881-30
1.67				
Before Exposure[a]	82.0	2.2	4.1	881-29
After Exposure	83.4	2.8	3.4	881-27
	75.8	2.4	4.8	↓
	78.6	2.8	4.8	
2.50				
Before Exposure[a]	66.2	1.8	4.1	881-44
After Exposure	69.6	1.6	4.1	881-42
	76.5	2.4	4.1	↓
	55.8	1.4	4.8	

(a) Highest single strength value in this group shown.

TABLE X (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 209 HOURS AT 600°F

Moles of HFDE, n	Ult. Tensile Strength, ksi	Total Elong., %	Mod. of Elasticity, msi	Ident.
1.30				
Before Exposure[a]	11.8	2.5	0.6	881-63
After Exposure	11.8	2.7	0.6	881-30
1.67				
Before Exposure[a]	11.9	2.2	0.6	881-29
After Exposure	12.1	2.8	0.5	881-27
	11.0	2.4	0.7	↓
	11.4	2.8	0.7	↓
2.50				
Before Exposure[a]	9.6	1.8	0.6	881-44
After Exposure	10.1	1.6	0.6	881-42
	11.1	2.4	0.6	↓
	8.1	1.4	0.7	↓

(a) Highest single strength value in this group shown.

TABLE XI (S.I. UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 382 HOURS AT 316°C

Moles of HFDE, n	Ult. Tensile Strength, MPa	Total Elong., %	Mod. of Elasticity, GPa	Ident.
1.30				
Before Exposure[a]	81.4	2.5	4.1	881-63
After Exposure	67.6	1.9	5.5	881-30
	78.6	2.2	5.5	881-30
1.67				
Before Exposure[a]	82.0	2.2	4.1	881-29
After Exposure	80.7	2.5	4.8	881-27
	76.5	2.3	4.1	↓
	79.3	2.5	4.1	↓
2.50				
Before Exposure[a]	66.2	1.8	4.1	881-44
After Exposure	39.3	0.9	4.8	881-44
	62.1	1.9	4.1	881-44
	78.6	2.6	5.5	881-42

(a) Highest single strength value in this group shown.

TABLE XI (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 382 HOURS AT 600°F

Moles of HFDE, n	Ult. Tensile Strength, ksi	Total Elong., %	Mod. of Elasticity, msi	Ident.
1.30				
Before Exposure[a]	11.8	2.5	0.6	881-63
After Exposure	9.8	1.9	0.8	881-30
	11.4	2.2	0.8	881-30
1.67				
Before Exposure[a]	11.9	2.2	0.6	881-29
After Exposure	11.7	2.5	0.7	881-27
	11.1	2.3	0.6	↓
	11.5	2.5	0.6	↓
2.50				
Before Exposure[a]	9.6	1.8	0.6	881-44
After Exposure	5.7	0.9	0.7	881-44
	9.0	1.9	0.6	881-44
	11.4	2.6	0.8	881-42

(a) Highest single strength value in this group shown.

TABLE XII (S.I. UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 572 HOURS AT 316°C

Moles of HFDE, n	Ult. Tensile Strength, MPa	Total Elong., %	Mod. of Elasticity, GPa	Ident.
1.30				
Before Exposure[a]	81.4	2.5	4.1	881-63
After Exposure[b]	20.7	0.5	4.1	881-34
	26.2	0.6	4.1	↓
	24.1	0.5	4.8	↓
1.67				
Before Exposure[a]	82.0	2.2	4.1	881-29
After Exposure	75.8	2.5	4.1	881-26
	45.5	1.3	4.1	↓
	40.7	1.2	4.1	↓
2.50				
Before Exposure[a]	66.2	1.8	4.1	881-44
After Exposure	83.4	2.6	4.1	881-42
	73.8	2.1	4.1	↓
	86.2	3.1	4.8	↓

(a) Highest single strength value in this group shown.

(b) All of these specimens failed in the tensile grips and are therefore not considered to be representative.

TABLE XII (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 572 HOURS AT 600°F

Moles of HFDE, n	Ult. Tensile Strength, ksi	Total Elong., %	Mod. of Elasticity, msi	Ident.
1.30				
Before Exposure[a]	11.8	2.5	0.6	881-63
After Exposure[b]	3.0	0.5	0.6	881-34
	3.8	0.6	0.6	↓
	3.5	0.5	0.7	↓
1.67				
Before Exposure[a]	11.9	2.2	0.6	881-29
After Exposure	11.0	2.5	0.6	881-26
	6.6	1.3	0.6	↓
	5.9	1.2	0.6	↓
2.50				
Before Exposure[a]	9.6	1.8	0.6	881-44
After Exposure	12.1	2.6	0.6	881-42
	10.7	2.1	0.6	↓
	12.5	3.1	0.7	↓

(a) Highest single strength value in this group shown.

(b) All of these specimens failed in the tensile grips and are therefore not considered to be representative.

TABLE XIII (S.I. UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 1000 HOURS AT 316°C

Moles of HFDE, n	Ult. Tensile Strength, MPa	Total Elong., %	Mod. of Elasticity, GPa	Ident.
1.30				
Before Exposure[(a)]	81.4	2.5	4.1	881-63
After Exposure	63.4	1.6	4.8	881-30
	64.1	2.0	5.5	↓
	72.4	1.5	4.8	
1.67				
Before Exposure[(a)]	82.0	2.2	4.1	881-29
After Exposure	60.0	1.9	3.4	881-29
	72.4	1.9	4.1	↓
	56.5	2.1	4.1	
2.50				
Before Exposure[(a)]	66.2	1.8	4.1	881-44
After Exposure	57.2	1.6	4.8	881-44
	34.5	0.8	5.5	↓
	33.8	0.9	4.1	

(a) Highest single strength value in this group.

TABLE XIII (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE TENSILE PROPERTIES OF PMR-II
NEAT RESIN SPECIMENS AFTER 1000 HOURS AT 600°F

Moles of HFDE, n	Ult. Tensile Strength, ksi	Total Elong., %	Mod. of Elasticity, msi	Ident.
1.30				
Before Exposure[a]	11.8	2.5	0.6	881-63
After Exposure	9.2	1.6	0.7	881-30
	9.3	2.0	0.8	↓
	10.5	1.5	0.7	↓
1.67				
Before Exposure[a]	11.9	2.2	0.6	881-29
After Exposure	8.7	1.9	0.5	881-29
	10.5	1.9	0.6	↓
	8.2	2.1	0.6	↓
2.50				
Before Exposure[a]	9.6	1.8	0.6	881-44
After Exposure	8.3	1.6	0.7	881-44
	5.0	0.8	0.8	↓
	4.9	0.9	0.6	↓

(a) Highest single strength value in this group.

TABLE XIV (S.I. UNITS)

232°C TENSILE STRENGTH OF PMR-II NEAT RESIN SPECIMENS AFTER EXPOSURE TO 316°C

Moles of HFDE, n	Before Exposure[a] Strength MPa	Ident.	After 209 hrs Strength MPa	Ident.	After 382 hrs Strength MPa	Ident.	After 572 hrs Strength MPa	Ident.	After 1000 hrs Strength MPa	Ident.
1.30	49.6	881-63	46.2	881-34	46.9	881-30	25.5	881-34	34.5	881-30
			34.5	881-34	45.5	881-30	20.7	↓	52.4	↓
							44.8	↓	49.0	↓
1.67	51.7	881-29	55.2	881-27	51.7	881-27	52.4	881-26	48.3	881-29
			51.7	↓	58.6	↓	58.6	881-27	51.7	↓
			53.1	↓	56.5	↓	47.6	881-29	38.6	↓
2.50	38.6	881-44	49.6	881-42	51.0	881-42	44.8	881-42	35.9	881-44
			41.4	↓	50.3	↓	46.9	↓	25.5	↓
			39.3	↓	50.3	↓	40.0	↓	–	↓

(a) Highest single strength value in this group shown.

TABLE XIV (U.S. CUSTOMARY UNITS)

450°F TENSILE STRENGTH OF PMR-II NEAT RESIN SPECIMENS AFTER EXPOSURE TO 600°F

Moles of HFDE, n	Before Exposure[a] Strength ksi	Ident.	After 209 hrs Strength ksi	Ident.	After 382 hrs Strength ksi	Ident.	After 572 hrs Strength ksi	Ident.	After 1000 hrs Strength ksi	Ident.
1.30	7.2	881-63	6.7	881-34	6.8	881-30	3.7	881-34	5.0	881-30
			5.0	881-34	6.6	881-30	3.0	↓	7.6	↓
							6.5	↓	7.1	↓
1.67	7.5	881-29	8.0	881-27	7.5	881-27	7.6	881-26	7.0	881-29
			7.5	↓	8.5	↓	8.5	881-27	7.5	↓
			7.7	↓	8.2	↓	6.9	881-29	5.6	↓
2.50	5.6	881-44	7.2	881-42	7.4	881-42	6.5	881-42	5.2	881-44
			6.0	↓	7.3	↓	6.8	↓	3.7	↓
			5.7	↓	7.3	↓	5.8	↓	-	↓

(a) Highest single strength value in this group shown.

TABLE XV

PERCENT DIMENSIONAL CHANGE OF PMR-II (n = 1.67)
NEAT RESIN MOLDINGS AFTER 192 HOURS AT 65°C (150°F)/97% RELATIVE HUMIDITY

	Postcured 881-26		Non-Postcured 881-48	
Identification	Thickness % Increase	Width % Increase	Thickness % Increase	Width % Increase
Sample 1	0.6	0.4	0.8	0.5
Sample 2	0.9	0.5	-0-	0.3
Sample 3	1.0	0.5	-0-	0.3
Avg.	0.8	0.5	0.3	0.4

TABLE XVI (S.I. UNITS)

ROOM TEMPERATURE AND 232°C TENSILE PROPERTIES OF PMR-II (n = 1.67)
NEAT RESIN SPECIMENS AFTER EXPOSURE TO 97% RELATIVE HUMIDITY FOR EIGHT DAYS

Humidity Exposure	Postcured	Test Temp. °C	Ult. Tensile Strength, MPa	Total Elongation, %	Mod. of Elasticity, GPa	Ident.
Before Exposure[(a)]	Yes	23	82.0	2.2	4.1	881-29
After Exposure	Yes		68.9	2.1	4.1	881-26
			73.1	2.2	4.1	↓
			62.7	1.6	4.8	
Before Exposure[(a)]	No		55.8	1.7	4.1	881-48
After Exposure	No		37.2	1.0	4.1	881-48
			38.6	0.9	4.1	↓
		↓	39.3	0.9	4.1	
Before Exposure[(a)]	Yes	232	51.7	-	-	881-29
After Exposure	Yes		49.6	-	-	881-26
			51.7			↓
			46.9			
Before Exposure[(a)]	No		31.0	-	-	881-48
After Exposure	No		24.1	-	-	881-48
			26.9			↓
		↓	33.1			

(a) Highest single strength value in this group shown.

(-) Humidity chamber temperature of 65°C.

TABLE XVI (U.S. CUSTOMARY UNITS)

ROOM TEMPERATURE AND 450°F TENSILE PROPERTIES OF PMR-II (n = 1.67)
NEAT RESIN SPECIMENS AFTER EXPOSURE TO 97% RELATIVE HUMIDITY FOR EIGHT DAYS

Humidity Exposure	Postcured	Test Temp. °F	Ult. Tensile Strength, ksi	Total Elongation, %	Mod. of Elasticity, msi	Ident.
Before Exposure[a]	Yes	73	11.9	2.2	0.6	881-29
After Exposure	Yes		10.0	2.1	0.6	881-26
			10.6	2.2	0.6	↓
			9.1	1.6	0.7	↓
Before Exposure[a]	No		8.1	1.7	0.6	881-48
After Exposure	No		5.4	1.0	0.6	881-48
			5.6	0.9	0.6	↓
		↓	5.7	0.9	0.6	↓
Before Exposure[a]	Yes	450	7.5	-	-	881-29
After Exposure	Yes		7.2	-	-	881-26
			7.5			↓
			6.8			↓
Before Exposure[a]	No		4.5	-	-	881-48
After Exposure	No.		3.5	-	-	881-48
			3.9			↓
		↓	4.8			↓

(a) Highest single strength value in this group shown.

(-) Humidity chamber temperature of 65°C (150°F).

TABLE XVII

GLASS TRANSITION TEMPERATURES OF
PMR-II NEAT RESIN MOLDINGS

Moles of HFDE, n	Glass Transition Temp., Tg(a) °C	°F	Mold Cycle(b)	Postcure	Treatment	Identity
1.30	383	721	A	Yes	-	881-34
1.67	370	698	A	↓	-	881-29
1.67	370	698	B	↓	-	881-46
2.50	359	678	B	↓	-	881-44
1.67	338	640	A	No	-	881-19
1.67	354	669	B	No	-	881-48
1.67	355	671	B	No	Humidity(c) Exposure	881-48
1.67	367	693	A	Yes	Humidity(c) Exposure	881-26

(a) Tg determined by Thermo-Mechanical Analysis (TMA) at 10°C/min. under nitrogen with a 4 gm load on the probe.

(b) Cycle A held 1 hour in die at 316°C; cycle B held 3 hours in die at 316°C.

(c) Humidity exposure was 192 hours at 65°C/97% RH.

TABLE XVIII

CHAR YIELD OF VARIOUS NEAT RESINS

Material	Avg. Char Yield, w/o	Log No.	Char Appearance	Nominal Sample Dimensions (mm) Lgt.	Width	Thick.
PMR-15	66.0	881-68	Sound	25.4	25.4	1.7
PMR-II n = 1.30	51.9	881-63	Blistered			
PMR-II n = 1.67	54.1	881-46				
PMR-II n = 2.50	54.0	881-45				
NR-059X	56.8	833-40				1.6
Epoxy-Novolac[(a)] & Tonox 60/40	33.5	--	Sooty Exterior		15.9	3.0

Notes: (-) Char yield values represent average of three samples.
(-) Char cycle terminated after four hours at 816°C (1500°F).
(-) Nominal sample weight = 4 grams.
(-) All polyimide specimens postcured 16 hours at 316°C (600°F).
(-) Epoxy-novolac specimens postcured 16 hours at 149°C (300°F).
(a) Actual composition:

50 parts	DER-331	(Liquid epoxy)
50 parts	DEN-438	(Epoxy-novolac)
20 parts	Tonox 60/40	(aromatic amine mixture)

TABLE XIX (S.I. UNITS)

SHORT BEAM SHEAR STRENGTH OF
PMR-II/C-3000 CLOTH LAMINATES

		n = 1.67 Lam. Ident. 881-54		n = 2.50 Lam. Ident. 881-84	
		Not Postcured	Postcured	Not Postcured	Postcured
RT Short Beam Shear Stg. (MPa)		64.1	58.6	80.0	80.0
		67.6	57.2	77.2	78.6
		66.2	62.1	79.3	73.8
	Avg	66.2	59.3	78.6	77.2
316°C Short Beam Shear Stg. (MPa)		28.3	30.3	25.5	27.6
		26.9	29.6	24.1	25.5
		27.6	31.0	22.8	24.8
	Avg	27.6	30.3	24.1	26.2

Notes: (-) n = moles of HFDE
(-) Span-to-depth ratio of 4:1.
(-) Postcure of 16 hours at 316°C.
(-) Fiber volumes determined to be: 881-54, 58.3 v/o; 881-84, 61.0 v/o.

TABLE XIX (U.S. CUSTOMARY UNITS)

SHORT BEAM SHEAR STRENGTH OF
PMR-II/C-3000 CLOTH LAMINATES

		n = 1.67 Lam. Ident. 881-54		n = 2.50 Lam. Ident. 881-84	
		Not Postcured	Postcured	Not Postcured	Postcured
RT Short Beam Shear Stg. (ksi)		9.3	8.5	11.6	11.6
		9.8	8.3	11.2	11.4
		9.6	9.0	11.5	10.7
	Avg	9.6	8.6	11.4	11.2
600°F Short Beam Shear Stg. (ksi)		4.1	4.4	3.7	4.0
		3.9	4.3	3.5	3.7
		4.0	4.5	3.3	3.6
	Avg	4.0	4.4	3.5	3.8

Notes: (-) n = moles of HFDE
(-) span-to-depth ratio of 4:1
(-) Postcure of 16 hours at 600°F
(-) Fiber volumes determined to be: 881-54, 58.3 v/o; 881-84, 61.0 v/o

TABLE XX (S.I. UNITS)

FLEXURAL PROPERTIES OF PMR-II/C-3000 CLOTH LAMINATES

		n = 1.67 Lam. Ident. 881-54				n = 2.50 Lam. Ident. 881-84			
		Not Postcured		Postcured		Not Postcured		Postcured	
		Stg. (MPa)	Mod. (GPa)	Stg. (MPa)	Mod. (GPa)	Stg. (MPa)	Mod. (GPa)	Stg. (MPa)	Mod. (GPa)
RT		914	72.4	1122	73.8	1138	84.8	987	77.9
		951	71.7	1140	76.5	1076	80.0	1071	80.7
		1036	74.5	1064	73.8	1063	79.3	1083	76.5
	Avg	967	73.1	1109	74.5	1093	81.4	1047	78.6
316°C		681	66.2	797	73.8	412	63.4	622	72.4
		696	65.5	774	71.0	498	68.3	651	73.8
		738	73.1	759	71.7	532	70.3	667	76.5
	Avg	705	68.3	777	72.4	481(a)	67.6	647	74.5

Notes: (a) Evidence of blistering from rapid rise to 316°C.
(-) n = moles of HFDE.
(-) Span-to-depth ratio of 33:1.
(-) Postcure of 16 hours at 316°C.
(-) Fiber volumes determined to be: 881-54, 58.3 v/o; 881-84, 61.0 v/o.

TABLE XX (U.S. CUSTOMARY UNITS)

FLEXURAL PROPERTIES OF PMR-II/C-3000 CLOTH LAMINATES

		n = 1.67 Lam. Ident. 881-54				n = 2.50 Lam. Ident. 881-84			
		Not Postcured		Postcured		Not Postcured		Postcured	
		Stg. (ksi)	Mod. (msi)	Stg. (ksi)	Mod. (msi)	Stg. (ksi)	Mod. (msi)	Stg. (ksi)	Mod. (msi)
RT		132.5	10.5	162.7	10.7	165.1	12.3	143.1	11.3
		138.0	10.4	165.3	11.1	156.1	11.6	155.3	11.7
		150.3	10.8	154.3	10.7	154.2	11.5	157.1	11.1
	Avg	140.3	10.6	160.8	10.8	158.5	11.8	151.8	11.4
600°F		98.8	9.6	115.6	10.7	59.8	9.2	90.2	10.5
		100.9	9.5	112.3	10.3	72.2	9.9	94.4	10.7
		107.0	10.6	110.1	10.4	77.1	10.2	96.8	11.1
	Avg	102.2	9.9	112.7	10.5	69.7[(a)]	9.8	93.8	10.8

Notes: (a) Evidence of blistering from rapid rise to 600°F.
(-) n = moles of HFDE.
(-) Span-to-depth ratio of 33:1.
(-) Postcure of 16 hours at 600°F.
(-) Fiber volumes determined to be: 881-54, 58.3 v/o; 881-84, 61.0 v/o.

TABLE XXI

CELION-3000 FABRIC COMPOSITE PROPERTIES AS REPORTED BY THE VENDOR

COMPOSITE PROPERTIES WITH WOVEN CELION FABRIC

Fabric: Fiberite Style W-1133, 24 x 23 8 Harness Satin
Composite: 65 volume percent Celion 3000 in Fiberite 934 epoxy resin.

	Warp	Fil
Flex Strength, 10^3psi	136.7	131
Flex Strength, 10^3psi @ 350°F	117.2	100.7
Flex Modulus, 10^6psi	11.0	10.5
Flex Modulus, 10^6psi @ 350°F	10.7	10.1
ILSS, psi	9722	9881
ILSS, psi @ 350°F	7148	6690
Tensile Strength, 10^3psi	93.2	86
Tensile Modulus, 10^6psi	11.4	10.5

Celion 3000 - High Strength carbon fiber with 3000 filaments per strand.
The above properties were obtained on autoclave cured laminates by Fiberite Corporation.

TYPICAL CELION 3000/PMR II POLYIMIDE COMPOSITE PROPERTIES

	73°F		600°F	
	Unidirectional	Fabric	Unidirectional	Fabric
Flex Strength, 10^3psi	220 - 290	115	130 - 145	80
Flex Modulus, 10^6psi	17.5 - 21	9		
Interlaminar Shear Strength, 10^3psi	14 - 17.8	7	7 - 8	6

Celion 3000 - High Strength carbon fiber with 3000 filaments per strand.

TABLE XXII (S.I. UNITS)

PMR-II/FORTAFIL-3 UNIDIRECTIONAL COMPOSITE MECHANICAL PROPERTIES

	Not Postcured			Postcured		
	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa
RT	1706	125	77.2	1616	128	59.3
316°C	1262	119	31.7	1346	125	42.1

Notes:
(-) Laminate No. 881-95
(-) Fiber Volume = 64.7 v/o
(-) Postcure 16 hours at 316°C
(-) PMR-II; n = 1.67
(-) All values represent average of three determinations.
(-) Unidirectionally oriented panels tested at 0 degrees.
(-) Short beam shear span-to-depth ratio of 4:1.
(-) Flexure test span-to-depth ratio of 32:1.

TABLE XXII (U.S. CUSTOMARY UNITS)

PMR-II/FORTAFIL-3 UNIDIRECTIONAL COMPOSITE MECHANICAL PROPERTIES

	Not Postcured			Postcured		
	Flex. Stg. ksi	Flex. Mod. msi	SBS ksi	Flex. Stg. ksi	Flex. Mod. msi	SBS ksi
RT	247.4	18.1	11.2	234.4	18.5	8.6
600°F	183.0	17.3	4.6	195.2	18.2	6.1

Notes:
(-) Laminate No. 881-95
(-) Fiber Volume = 64.7 v/o
(-) Postcure 16 hours at 600°F
(-) PMR-II; n = 1.67
(-) All values represent average of three determinations
(-) Unidirectionally oriented panels tested at 0°
(-) Short beam shear span-to-depth ratio of 4:1
(-) Flexure test span-to-depth ratio of 32:1

TABLE XXIII

F-3 COMPOSITE PROPERTIES AS REPORTED BY THE VENDOR

TYPICAL UNIDIRECTIONAL COMPOSITE PROPERTIES

In a Typical Epoxy @ 60% fiber Volume

Flexural Strength (KSI)	215
Flexural Modulus (MSI)	18
Tensile Strength (KSI)	190
Compressive Strength (KSI)	190
Shear Strength (KSI - 4:1 short beam test)	12

TABLE XXIV (S.I. UNITS)

MECHANICAL PROPERTIES OF NON-POSTCURED NR-059X/C-3000 CLOTH LAMINATES

		Short Beam Shear Strength (MPa)	Flexural Properties	
			Strength (MPa)	Modulus (GPa)
RT		-	940	70.3
		-	943	69.6
	Avg	-	941	70.3
316°C		30.3	579	65.5
		27.6	574	68.9
		27.6	668	69.6
	Avg	28.3	607(a)	68.3

Notes: (a) Evidence of blistering from rapid rise to 316°C.
(-) Laminate identity 881-65.
(-) Shear span-to-depth ratio 4:1.
(-) Flexural span-to-depth ratio 33:1.

TABLE XXIV (U.S. CUSTOMARY UNITS)

MECHANICAL PROPERTIES OF NON-POSTCURED NR-059X/C-3000 CLOTH LAMINATES

		Short Beam Shear Strength (ksi)	Flexural Properties Strength (ksi)	Flexural Properties Modulus (msi)
RT		-	136.3	10.2
		-	136.7	10.1
	Avg	-	136.5	10.2
600°F		4.4	84.0	9.5
		4.0	83.3	10.0
		4.0	96.9	10.1
	Avg	4.1	88.1 (a)	9.9

Notes: (a) Evidence of blistering from rapid rise to 600°F.
(-) Laminate identity 881-65.
(-) Shear span-to-depth ratio 4:1.
(-) Flexural span-to-depth ratio 33:1.

TABLE XXV (S.I. UNITS)

MECHANICAL PROPERTIES OF POSTCURED NR-059X/C-3000 CLOTH LAMINATES

	NR-059X in the As-Received Condition Lam. Ident. 881-67			NR-059X after 5 Weeks Storage at -18°C(a) Lam. Ident. 881-79		
	SBS Stg. (MPa)	Flex. Stg. (MPa)	Flex. Mod. (GPa)	SBS Stg. (MPa)	Flex. Stg. (MPa)	Flex. Mod. (GPa)
RT	62.1	1020	71.7	62.7	1020	70.3
	55.2	1057	71.7	68.3	1054	74.5
	63.4	1007	72.4	71.7	1016	77.2
Avg	60.0	1028	71.7	67.6	1030	73.8
316°C	36.5	780	67.6	26.2	665	68.3
	31.7	787	68.3	31.0	663	66.9
	32.4	796	69.6	31.7	722	70.3
Avg	33.8	788	68.3	29.6	683	68.3

Notes: (-) Shear span-to-depth ratio 4:1.
(-) Flexure span-to-depth ratio 32:1.
(-) Postcure of 16 hours at 316°C.
(-) Fiber volumes determined to be: 881-67, 54.1 v/o; 881-79, 57.9 v/o.

(a) Specimens taken from area exhibiting clear C-scan.

TABLE XXV (U.S. CUSTOMARY UNITS)

MECHANICAL PROPERTIES OF POSTCURED NR-059X/C-3000 CLOTH LAMINATES

	NR-059X in the As-Received Condition Lam. Ident. 881-67			NR-059X after 5 Weeks Storage at 0°F(a) Lam. Ident. 881-79		
	SBS Stg. (ksi)	Flex. Stg. (ksi)	Flex. Mod. (msi)	SBS Stg. (ksi)	Flex. Stg. (ksi)	Flex. Mod. (msi)
RT	9.0	147.9	10.4	9.1	148.0	10.2
	8.0	153.3	10.4	9.9	152.9	10.8
	9.2	146.0	10.5	10.4	147.3	11.2
Avg	8.7	149.1	10.4	9.8	149.4	10.7
600°F	5.3	113.2	9.8	3.8	96.5	9.9
	4.6	114.2	9.9	4.5	96.2	9.7
	4.7	115.4	10.1	4.6	104.7	10.2
Avg	4.9	114.3	9.9	4.3	99.1	9.9

Notes: (-) Shear span-to-depth ratio 4:1.
(-) Flexure span-to-depth ratio 32:1.
(-) Postcure of 16 hours at 600°F.
(-) Fiber volumes determined to be: 881-67, 54.1 v/o; 881-79, 57.9 v/o.

(a) Specimens taken from area exhibiting clear C-scan.

TABLE XXVI (S.I. UNITS)

PMR-II/C-3000 BASELINE MECHANICAL COMPOSITE PROPERTIES

Lam. No.	Fiber Vol., v/o	RT Flex. Stg. MPa	RT Flex. Mod. GPa	RT SBS MPa	232°C Flex. Stg. MPa	232°C Flex. Mod. GPa	232°C SBS MPa	316°C Flex. Stg. MPa	316°C Flex. Mod. GPa	316°C SBS MPa
886-2	64.0	1127	83.4	72.4	1034	83.4	49.0	865	79.3	38.6
886-3	64.7	-	-	-	-	-	-	737	71.7	37.9
886-4	61.4	1063	77.9	73.1	971	77.9	51.7	-	-	-

Notes:
(-) All values represent average of three determinations.
(-) All laminates postcured 16 hours at 316°C.
(-) PMR-II: n = 1.67.
(-) C-3000 cloth laminates tested in warp direction.
(-) Span-to-depth ratios were 35:1 for flexure and 4:1 for short beam shear (SBS) testing.

TABLE XXVI (U.S. CUSTOMARY UNITS)

PMR-II/C-3000 BASELINE MECHANICAL COMPOSITE PROPERTIES

Lam. No.	Fiber Vol., v/o	RT			450°F			600°F		
		Flex. Stg. ksi	Flex. Mod. msi	SBS ksi	Flex. Stg. ksi	Flex. Mod. msi	SBS ksi	Flex. Stg. ksi	Flex. Mod. msi	SBS ksi
886-2	64.0	163.4	12.1	10.5	149.9	12.1	7.1	125.5	11.5	5.6
886-3	64.7	-	-	-	-	-	-	106.9	10.4	5.5
886-4	61.4	154.1	11.3	10.6	140.5	11.3	7.5	-	-	-

Notes:
(-) All values represent average of three determinations.
(-) All laminates postcured 16 hours at 600°F.
(-) PMR-II: n = 1.67.
(-) C-3000 cloth laminates tested in warp direction.
(-) Span-to-depth ratios were 35:1 for flexure and 4:1 for short beam shear (SBS) testing.

TABLE XXVII (S.I. UNITS)

PMR-II/F-3 BASELINE MECHANICAL COMPOSITE PROPERTIES

Lam. No.	Fiber Vol., v/o	RT			232°C			316°C		
		Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa
881-97	63.0	1661	130	78.6	1580	128	61.4	1389	123	48.3
881-98	63.8	-	-	-	-	-	-	1338	128	47.6
881-99	64.2	1600	127	75.2	1519	128	59.3	-	-	-

Notes:
(-) All values represent average of three determinations.
(-) All laminates postcured 16 hours at 316°C.
(-) Unidirectionally oriented panels tested at 0 degrees.
(-) Span-to-depth ratios were 33:1 for flexure and 4:1 for short beam shear (SBS) testing.

TABLE XXVII (U.S. CUSTOMARY UNITS)

PMR-II/F-3 BASELINE MECHANICAL COMPOSITE PROPERTIES

Lam. No.	Fiber Vol., v/o	RT			450°F			600°F		
		Flex. Stg. ksi	Flex. Mod. msi	SBS ksi	Flex.Stg. ksi	Flex. Mod. msi	SBS ksi	Flex. Stg. ksi	Flex. Mod. msi	SBS ksi
881-97	63.0	240.9	18.8	11.4	229.2	18.5	8.9	201.5	17.9	7.0
881-98	63.8	-	-	-	-	-	-	194.0	18.5	6.9
881-99	64.2	232.1	18.4	10.9	220.3	18.5	8.6	-	-	-

Notes:
(-) All values represent average of three determinations.
(-) All laminates postcured 16 hours at 600°F.
(-) Unidirectionally oriented panels tested at 0°.
(-) Span-to-depth ratios were 33:1 for flexure and 4:1 for short beam shear (SBS) testing.

TABLE XXVIII (S.I. UNITS)

316°C MECHANICAL PROPERTIES OF PMR-II/F-3
UNIDIRECTIONAL LAMINATES AFTER EXPOSURE AT 316°C

Laminate No.	Time at 316°C hours	Flex. Strength MPa	Flex. Strength % Retention	Flex. Modulus GPa	Short Beam Shear Strength MPa	Short Beam Shear Strength % Retention
881-97	0[a]	1389	100	123	48.3	100
-98	0[a]	1338	100	128	47.6	100
-98	300	1282	94	123	55.2	100
-97	600	1303	96	145	31.7	66
-98	1000	1149	84	145	25.5	54
-97	1500	431	32	103	-	-
-98	1500	-	-	-	24.1	50

Notes: (a) Postcured 16 hours at 316°C.

(-) PMR-II = n at 1.67.
(-) Values shown represent an average of three determinations.

TABLE XXVIII (U.S. CUSTOMARY UNITS)

600°F MECHANICAL PROPERTIES OF PMR-II/F-3
UNIDIRECTIONAL LAMINATES AFTER EXPOSURE AT 600°F

Laminate No.	Time at 600°F hours	Flex. Strength ksi	Flex. Strength % Retention	Flex. Modulus msi	Short Beam Shear Strength ksi	Short Beam Shear Strength % Retention
881-97	0[(a)]	201.5	100	17.9	7.0	100
-98	0[(a)]	194.0	100	18.5	6.9	100
-98	300	186.0	94	17.8	8.0	100
-97	600	189.0	96	21.1	4.6	66
-98	1000	166.6	84	21.0	3.7	54
-97	1500	62.5	32	15.0	-	-
-98	1500	-	-	-	3.5	50

Notes: (a) Postcured 16 hours at 600°F.

(-) PMR-II = n at 1.67.
(-) Values shown represent an average of three determinations.

TABLE XXIX (S.I. UNITS)

316°C MECHANICAL PROPERTIES OF PMR-II/C-3000
FABRIC LAMINATES AFTER EXPOSURE AT 316°C

Laminate No.	Time at 316°C hours	Flex. Strength MPa	Flex. Strength % Retention	Flex. Modulus GPa	Short Beam Shear Strength MPa	Short Beam Shear Strength % Retention
886-2	0[a]	865	100	79.3	38.6	100
-3	0[a]	737	100	71.7	37.9	100
-3	300	773	96	65.5	45.5	100
-2	600	532	66	84.1	24.8	64
-3	1000	261	33	66.9	17.2	45
-2	1500	163	20	37.2	-	-
-3	1500	-	-	-	7.6	20

Notes: (a) Postcured 16 hours at 316°C.

(-) PMR-II = n at 1.67.
(-) Values shown represent an average of three determinations.

TABLE XXIX (U.S. CUSTOMARY UNITS)

600°F MECHANICAL PROPERTIES OF PMR-II/C-3000
FABRIC LAMINATES AFTER EXPOSURE AT 600°F

Laminate No.	Time at 600°F hours	Flex. Strength ksi	Flex. Strength % Retention	Flex. Modulus msi	Short Beam Shear Strength ksi	Short Beam Shear Strength % Retention
886-2	0[a]	125.5	100	11.5	5.6	100
-3	0[a]	106.9	100	10.4	5.5	100
-3	300	112.1	96	9.5	6.6	100
-2	600	77.1	66	12.2	3.6	64
-3	1000	37.9	33	9.7	2.5	45
-2	1500	23.7	20	5.4	-	-
-3	1500	-	-	-	1.1	20

Notes: (a) Postcured 16 hours at 600°F.

(-) PMR-II = n at 1.67.
(-) Values shown represent an average of three determinations.

TABLE XXX (S.I. UNITS)

MECHANICAL PROPERTY DATA ON PMR-II
COMPOSITES AFTER MOISTURE EXPOSURE

	RT			232°C		
	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa	Flex. Stg. MPa	Flex. Mod. GPa	SBS MPa
PMR-II/F-3[a]						
Before Exposure	1600	127	75.2	1519	128	59.3
After Exposure	1730	128	69.6	1237	113	40.0
PMR-II/C-3000[b]						
Before Exposure	1062	78	73.1	969	78	51.7
After Exposure	1044	75	66.9	887	72	33.8

Notes: (a) Laminate 881-99, V_f = 64.2 v/o, thickness 2.3 mm.

(b) Laminate 886-4, V_f = 61.4 v/o, thickness 2.2 mm.

(-) All values represent average of three determinations.

TABLE XXX (U.S. CUSTOMARY UNITS)

MECHANICAL PROPERTY DATA ON PMR-II
COMPOSITES AFTER MOISTURE EXPOSURE

	RT			450°F		
	Flex. Stg.	Flex. Mod.	SBS	Flex. Stg.	Flex. Mod.	SBS
PMR-II/F-3[a]	ksi	msi	ksi	ksi	msi	ksi
Before Exposure	232.1	18.4	10.9	220.3	18.5	8.6
After Exposure	250.9	18.5	10.1	179.4	16.4	5.8
PMR-II/C-3000[b]						
Before Exposure	154.1	11.3	10.6	140.5	11.3	7.5
After Exposure	151.4	10.9	9.7	128.7	10.5	4.9

Notes: (a) Laminate 881-99, V_f = 64.2 v/o, thickness 0.089 inch.

(b) Laminate 886-4, V_f = 61.4 v/o, thickness 0.088 inch.

(-) All values represent average of three determinations.

TABLE XXXI

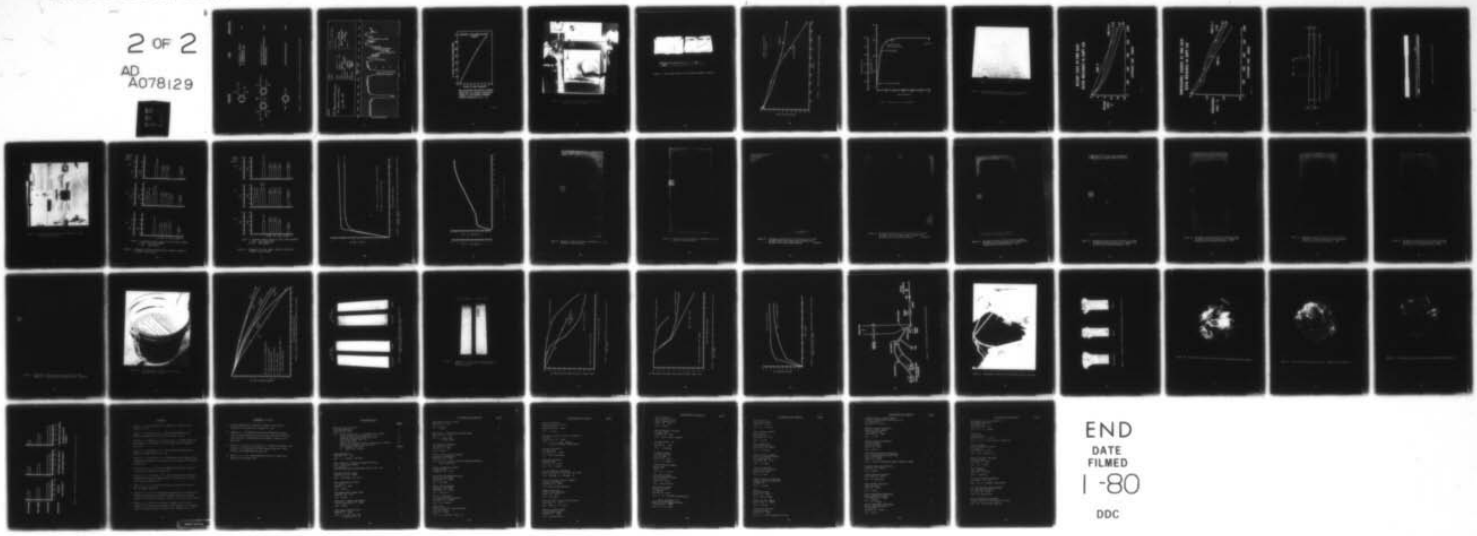
RESULTS OF BURNER EXPOSURE
TESTING OF COMPOSITES

Material		Weight Loss After Burn, %	Additional Weight Loss After Air Shock, %
PMR-15/C-3000		6.8	0.4
Lam 881-60		6.2	0.5
		7.6	0.3
		8.1	0.3
		7.2	0.3
	Avg	7.2	0.3
PMR-II/C-3000		10.0	0.8
Lam 881-53		10.1	0.9
		9.8	0.7
		10.5	0.8
		10.3	0.8
	Avg	10.1	0.8
Epoxy/Epoxy-Novolac		17.9	1.1
Lam 881-59		20.7	1.5
		21.8	1.7
		20.4	1.9
		20.4	1.4
	Avg	20.2	1.5
PMR-15/C-3000[(a)]		7.6	0.5
Lam 881-60		6.9	0.2
		6.4	0.3
	Avg	7.0	0.3

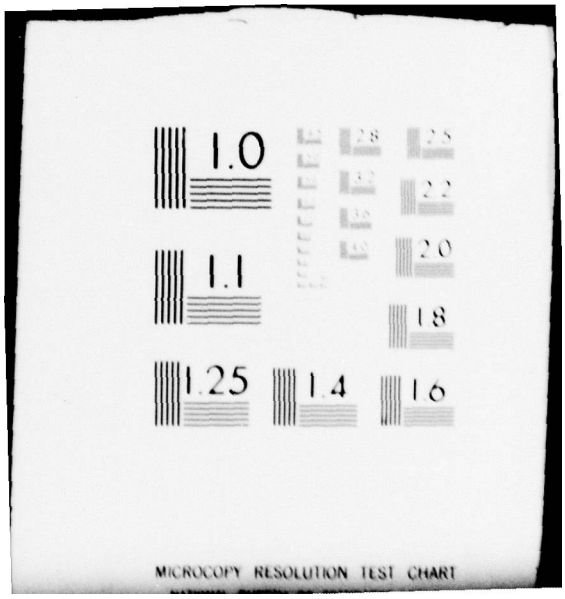
Note: (a) These three samples of same laminate were tested two weeks after initial tests to establish reproducibility of burner rig gages and regulators.

AD-A078 129 TRW EQUIPMENT GROUP CLEVELAND OHIO F/G 11/4
SECOND GENERATION PMR POLYIMIDE/FIBER COMPOSITES. (U)
OCT 79 P J CAVANO NAS3-21349
UNCLASSIFIED TRW-ER-7989F NASA -CR-159666 NL

2 OF 2
AD A078129



END
DATE FILMED
1-80
DDC


1.0
1.1
1.25
1.4
1.6
2.0
2.2
2.5
1.8
MICROCOPY RESOLUTION TEST CHART

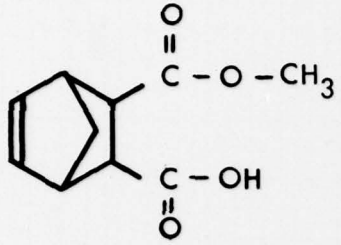
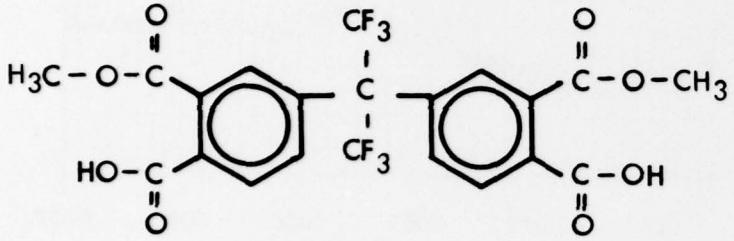
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5 - NORBORNENE - 2, 3 - DICARBOXYLIC ACID	NE
	DIMETHYLESTER OF 4, 4' - (HEXAFLUOROISOPROPYLIDENE)- BIS (PHTHALIC ACID)	HFDE
	PARA-PHENYLENEDIAMINE	PPDA

Figure 1. Monomers Used in the Preparation of Second Generation PMR Polyimides.

REMARKS

4,4'-(HEXAFLUOROISOPROPYLIDENE)-bis(PHTHALIC ANHYDRIDE).

m.p. 242-244

ORIGIN

PURITY

SPEED NORMAL ✓ FAST

SLITS NORMAL ✓ WIDE

PHASE Solid.

CONCENTRATION Mull

THICKNESS film

DATE 3/28/78

OPERATOR RSH.

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

SPECTRUM NO.

SAMPLE 1 HFDA
~~Lot# AB 785~~
3,396g.

SAMPLE 2

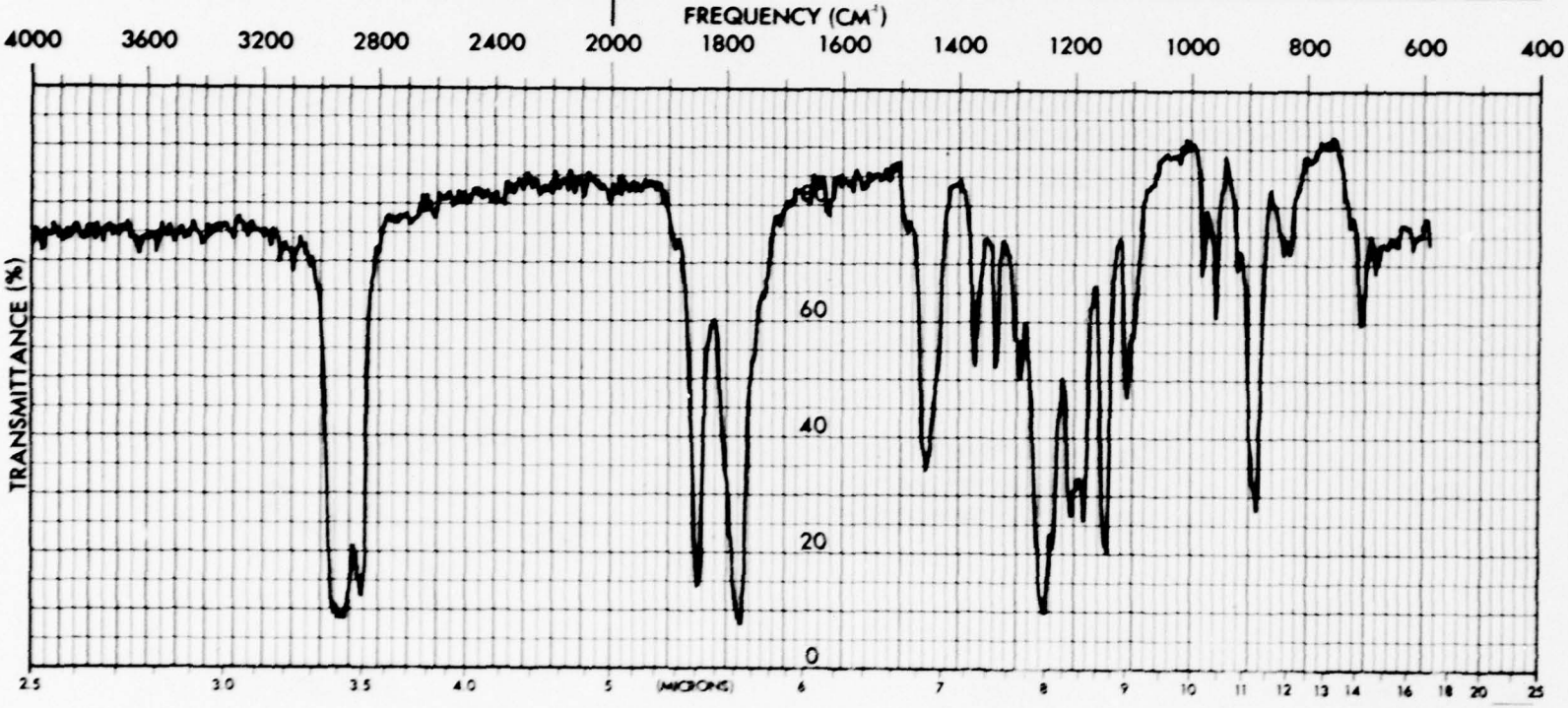
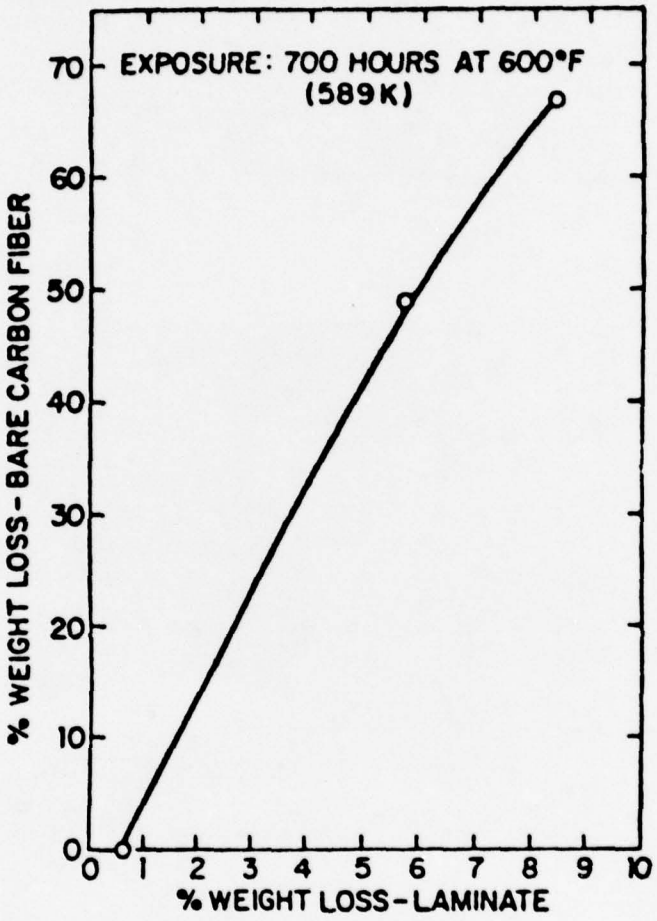


FIGURE 2. HFDA CERTIFICATION



RELATIONSHIP BETWEEN CARBON FIBER NR-150 BASED LAMINATE STABILITY AND BARE CARBON FIBER STABILITY (REF. 8)

Figure 3

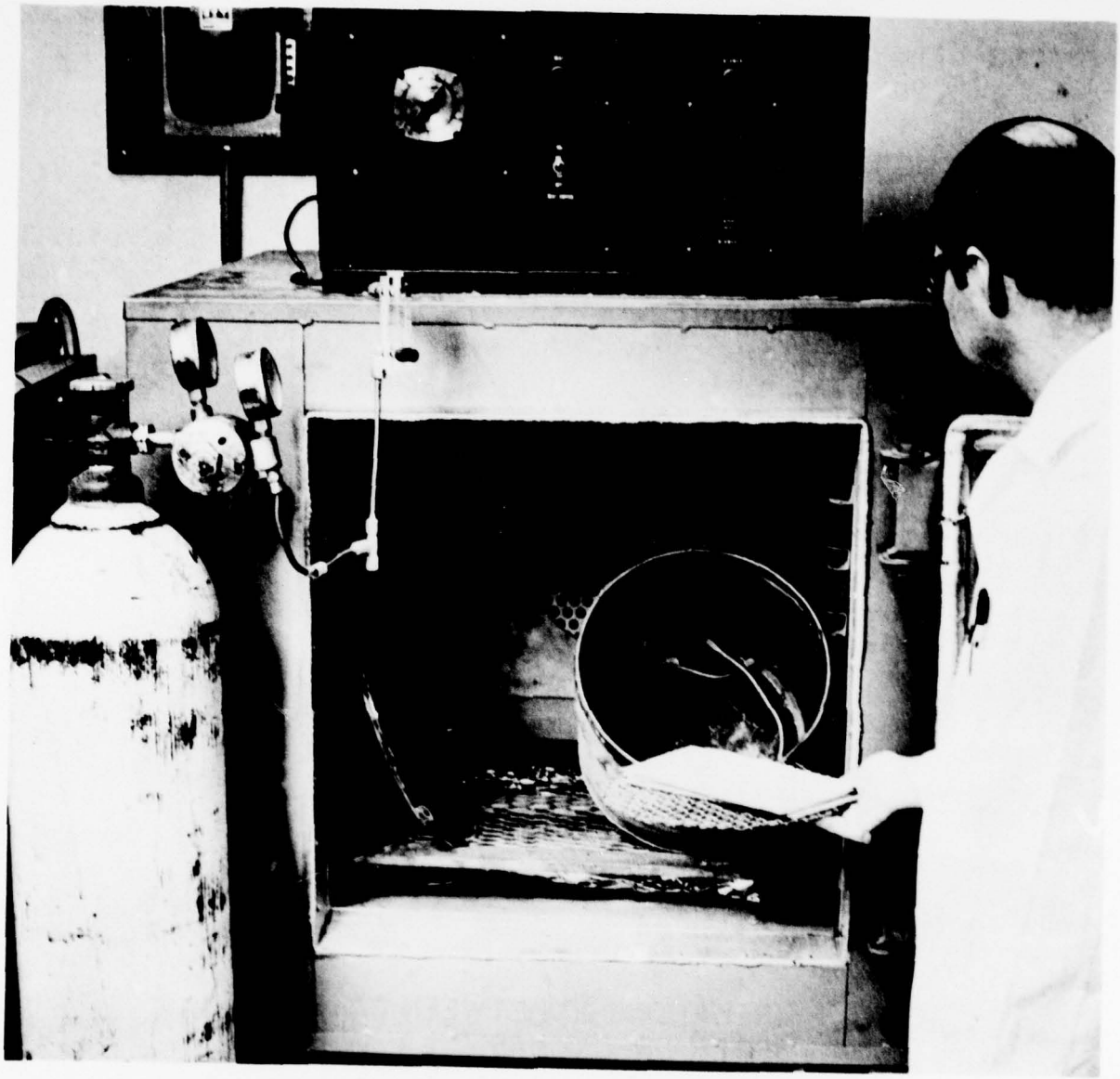


Figure 4. Isothermal Exposure Set-up Showing Air Source, Flow Meter and Inner Chamber.

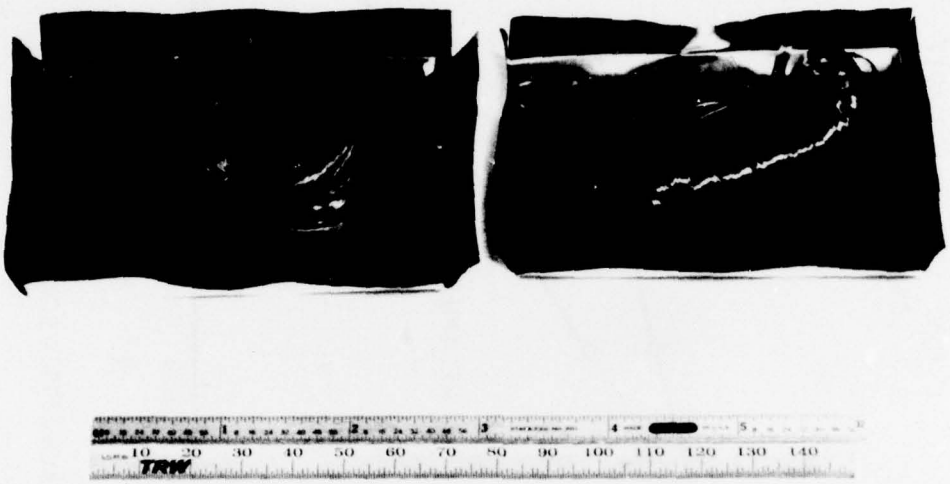


Figure 5. Fiber Samples Ready for Isothermal Gravimetric Analysis.

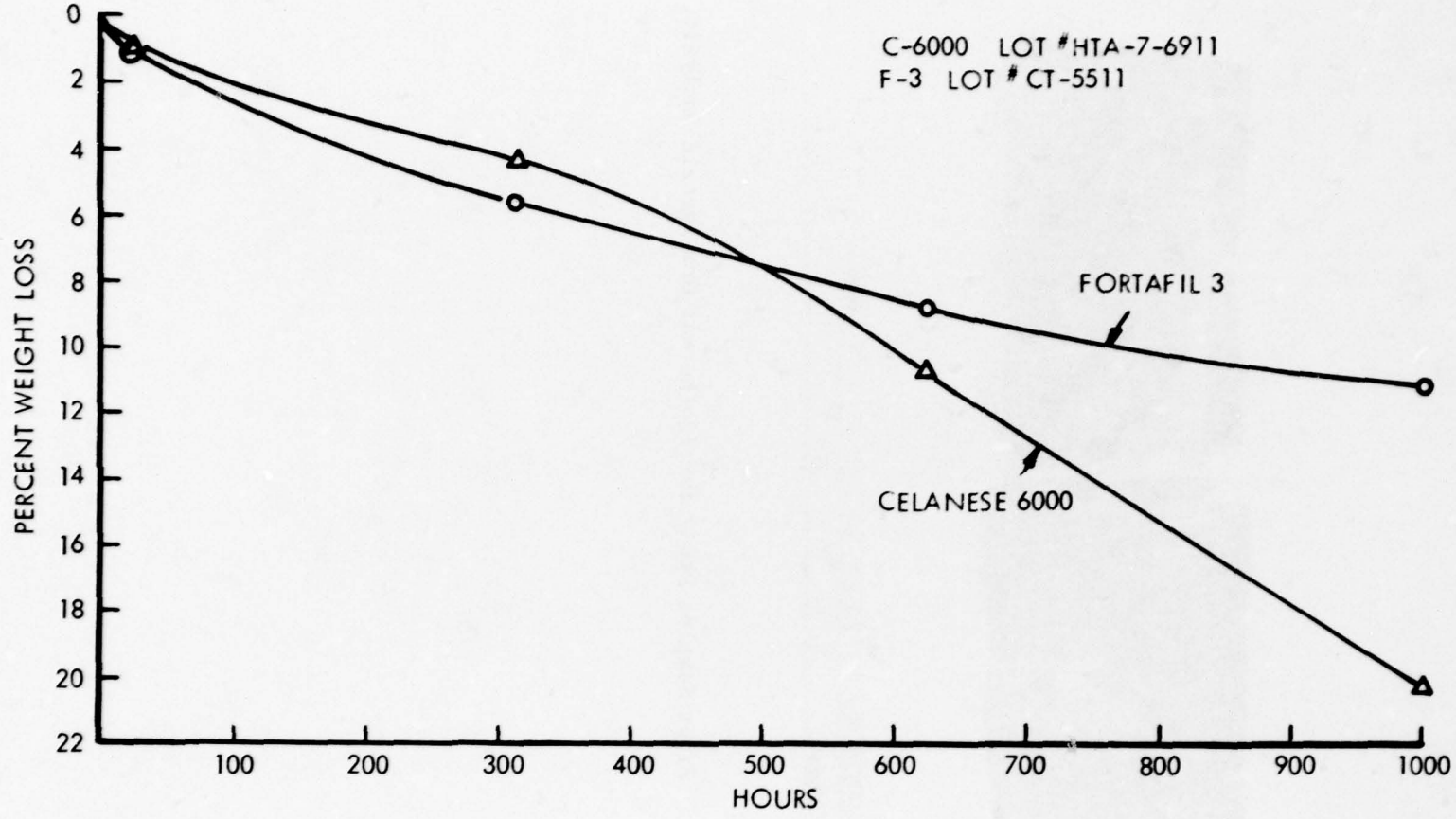


FIGURE 6. WEIGHT LOSS OF BARE CARBON FIBER TOWS AT 316°C (600°F)

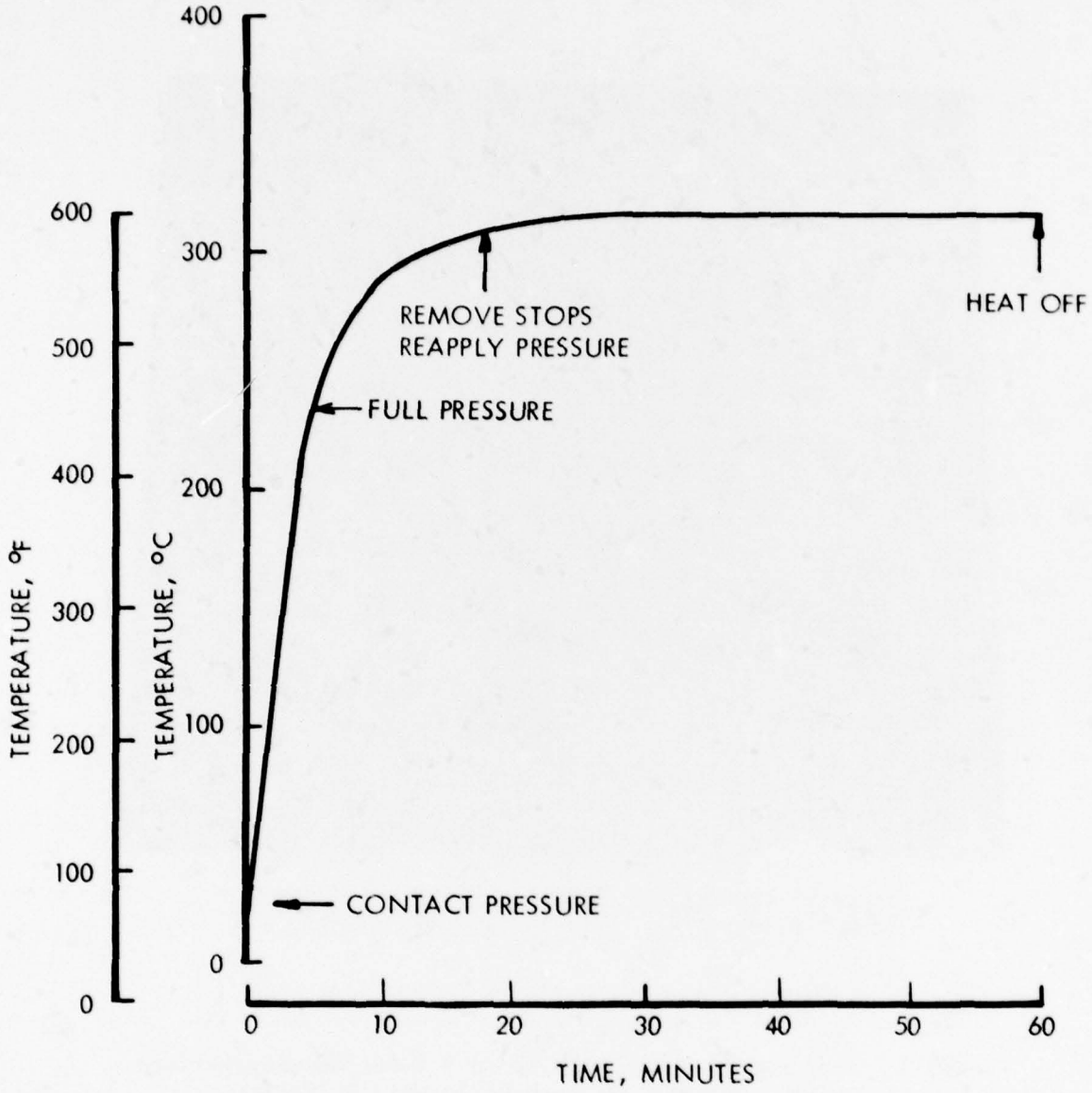


Figure 7. Mold Cycle for Neat PMR-II.

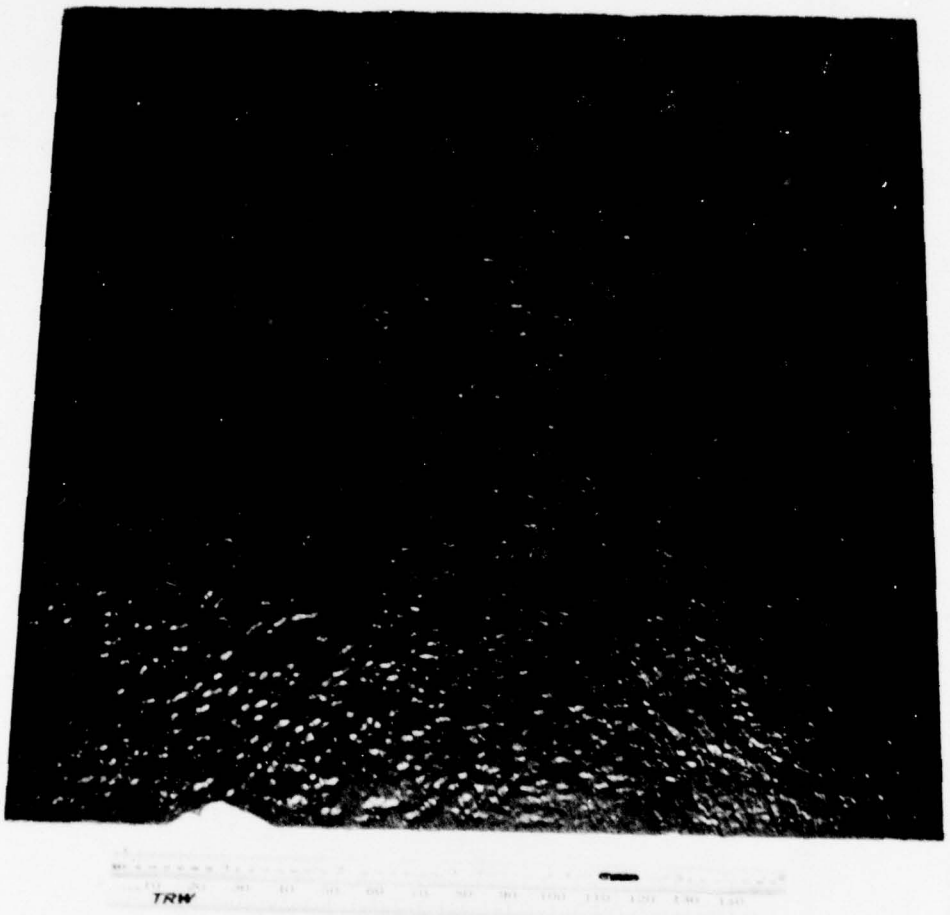


Figure 8. Neat PMR-II Resin Molding (n = 2.50) Showing Surface Defects Experienced with Early Molding Cycle.

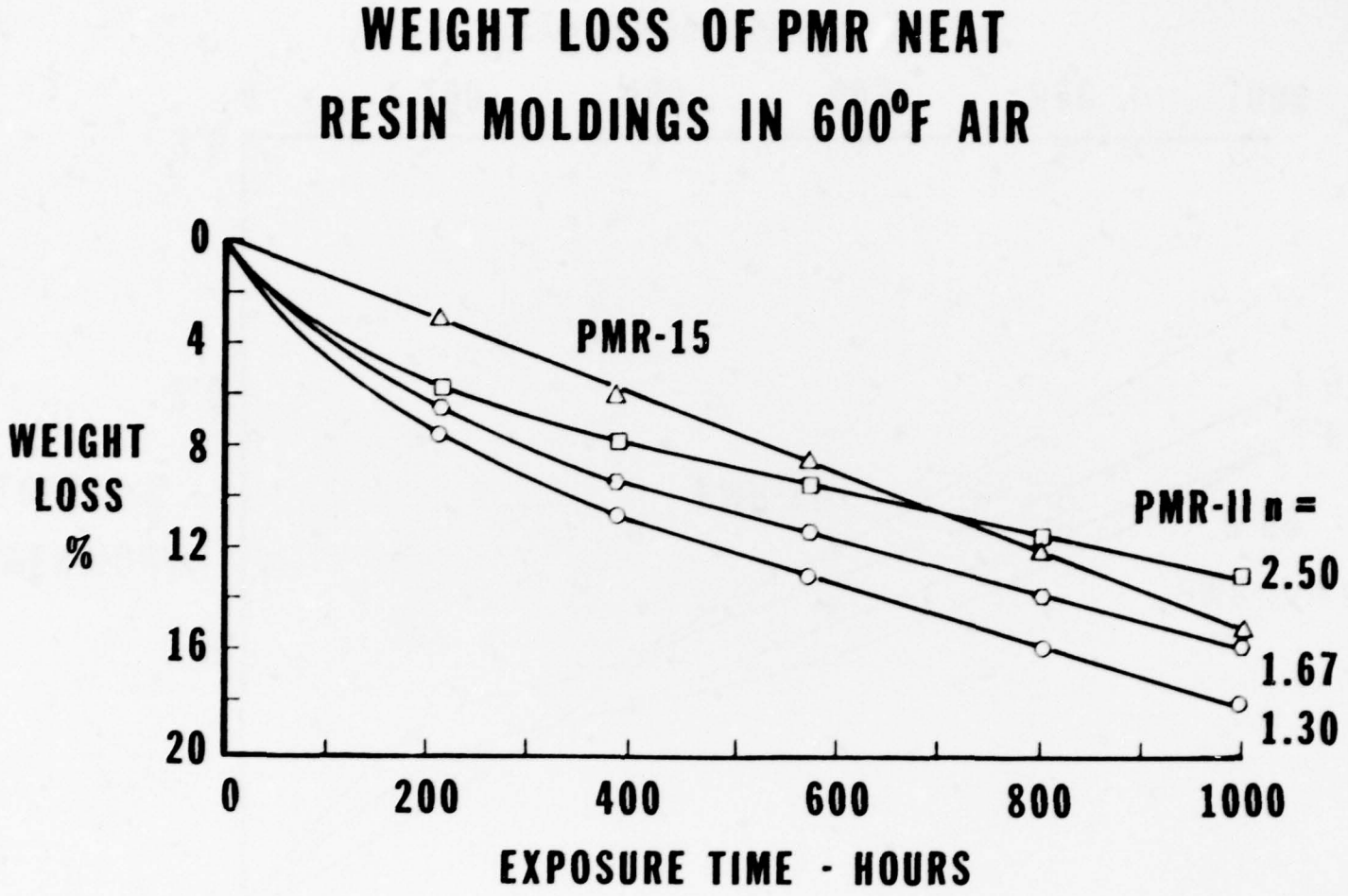

WEIGHT LOSS OF PMR NEAT
RESIN MOLDINGS IN 600°F AIR
WEIGHT LOSS %
0
4
8
12
16
20
PMR-15
PMR-II n =
2.50
1.67
1.30
0
200
400
600
800
1000
EXPOSURE TIME - HOURS

Figure 9.

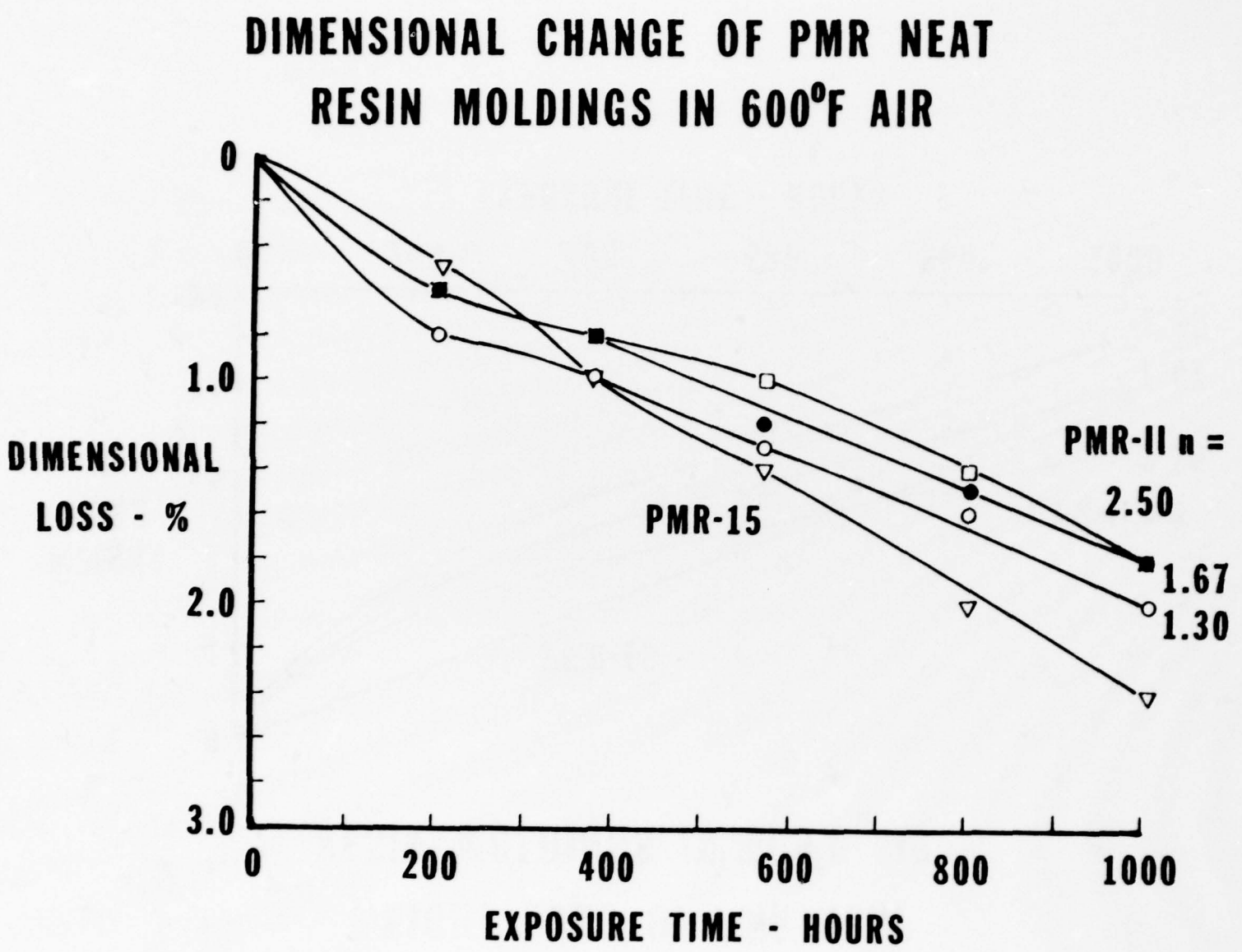
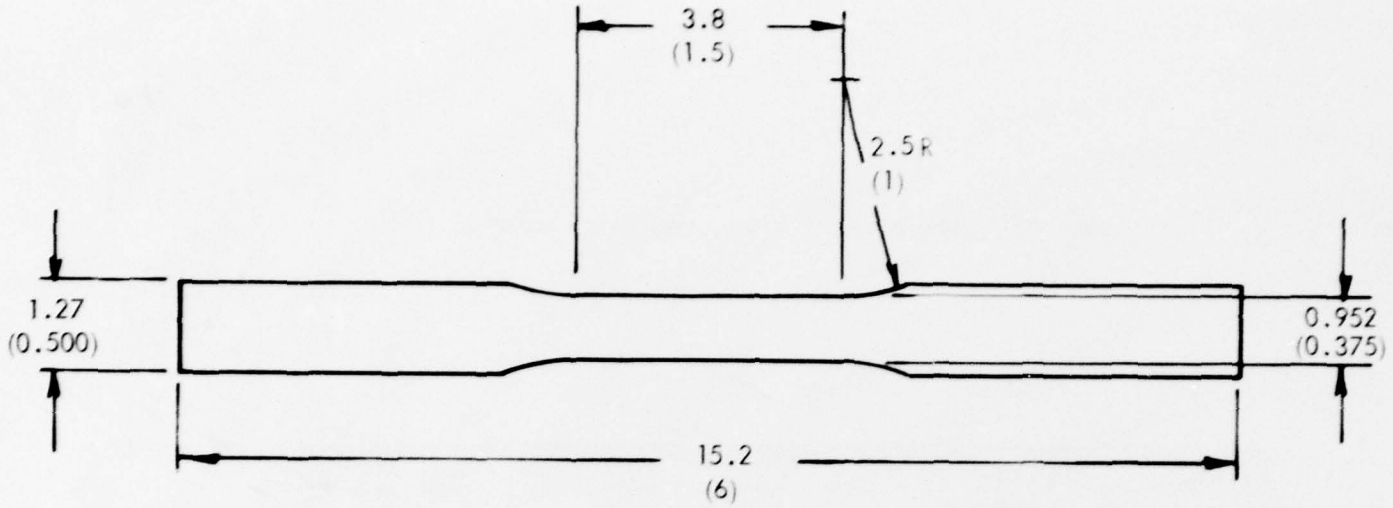

DIMENSIONAL CHANGE OF PMR NEAT RESIN MOLDINGS IN 600°F AIR
0
1.0
2.0
3.0
DIMENSIONAL LOSS - %
PMR-15
PMR-II n =
2.50
1.67
1.30
0
200
400
600
800
1000
EXPOSURE TIME - HOURS

Figure 10.



DIMENSIONS IN cm (INCHES)

THICKNESS NOMINALLY 1.27 TO 152 mm (0.050 - 0.060 INCHES)

FIGURE 11. NEAT RESIN TENSILE SPECIMEN



Figure 12. Neat Resin Tensile Test Specimen.

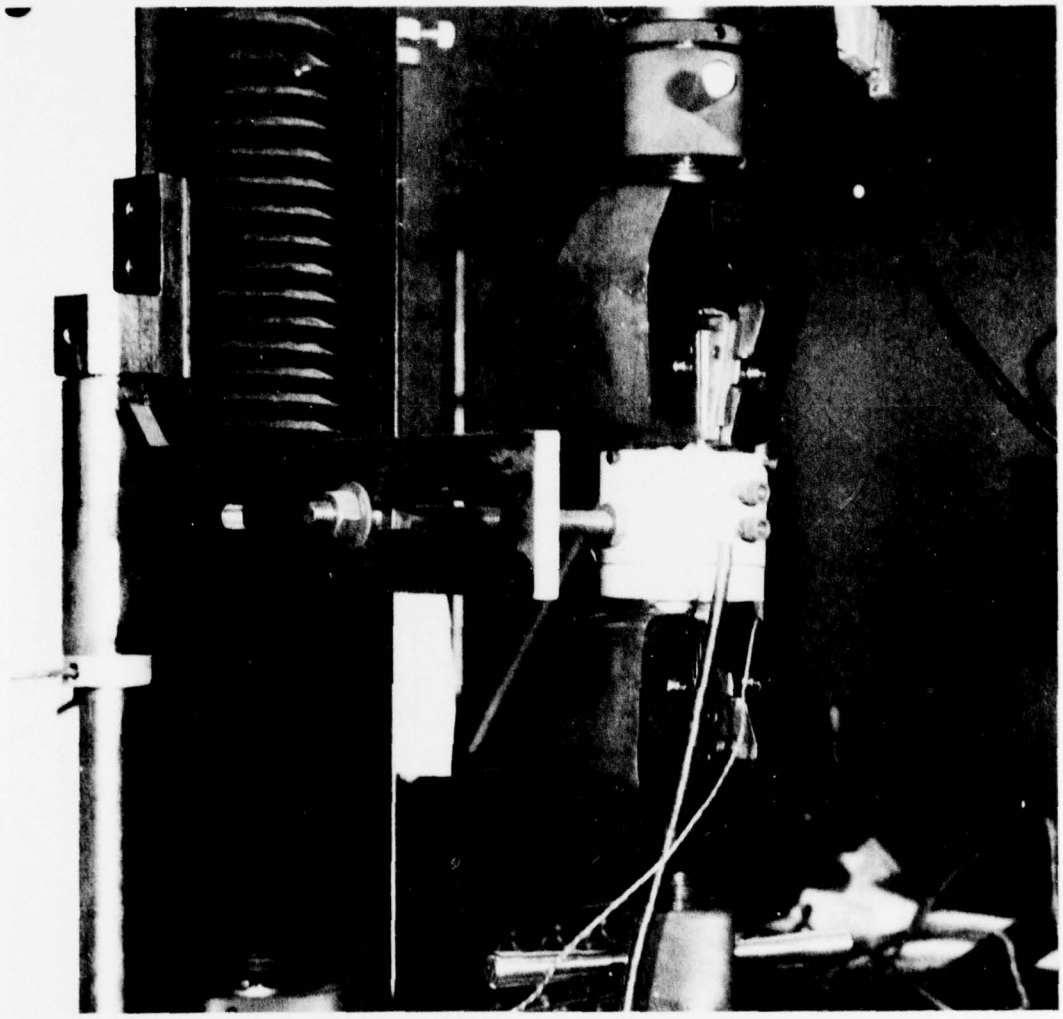
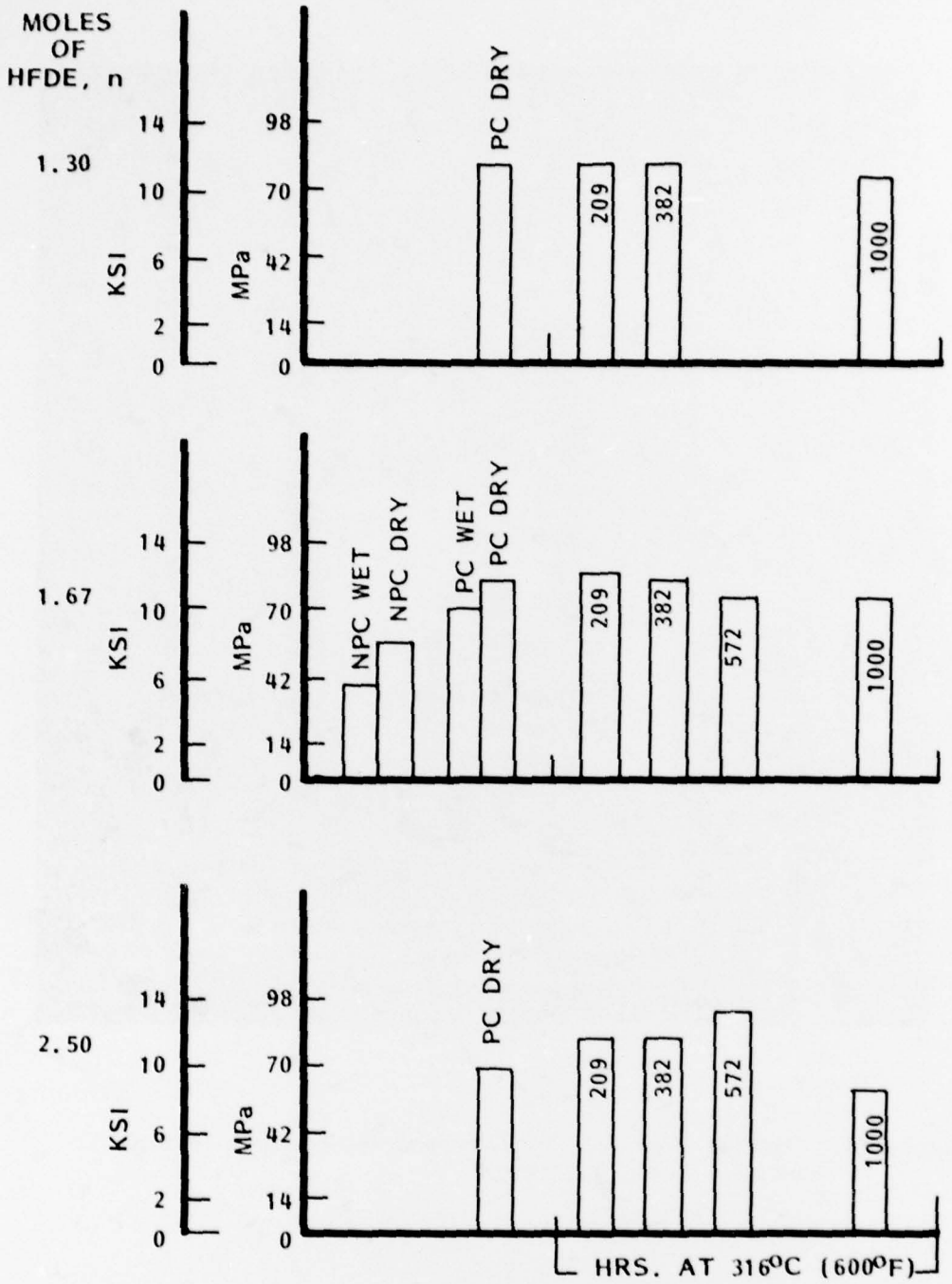
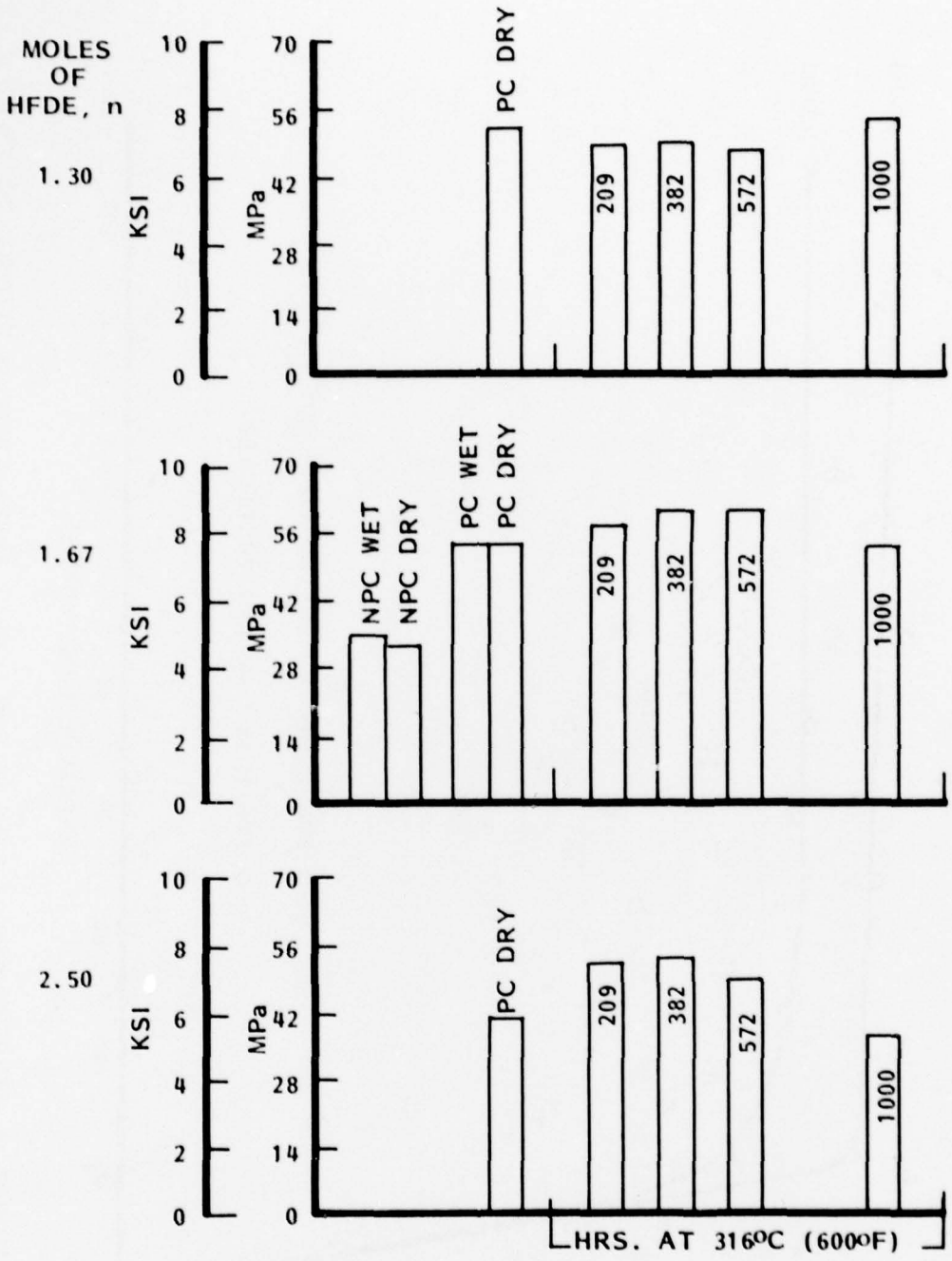


Figure 13. Special Oven for the Elevated Temperature Testing of Neat Resin Specimens.



NOTE: (-) HIGHEST SINGLE VALUE IN EACH GROUP SHOWN
(-) NPC = NOT POSTCURED
(-) PC = POSTCURED

FIGURE 14 SUMMARY OF ROOM TEMPERATURE TENSILE STRENGTH OF PMR-II NEAT RESIN.



NOTE: (-) HIGHEST SINGLE VALUE IN EACH GROUP SHOWN.
(-) NPC = NOT POSTCURED
(-) PC = POSTCURED

FIGURE 15 SUMMARY OF 232°C (450°F) TENSILE STRENGTH OF PMR-II NEAT RESIN.

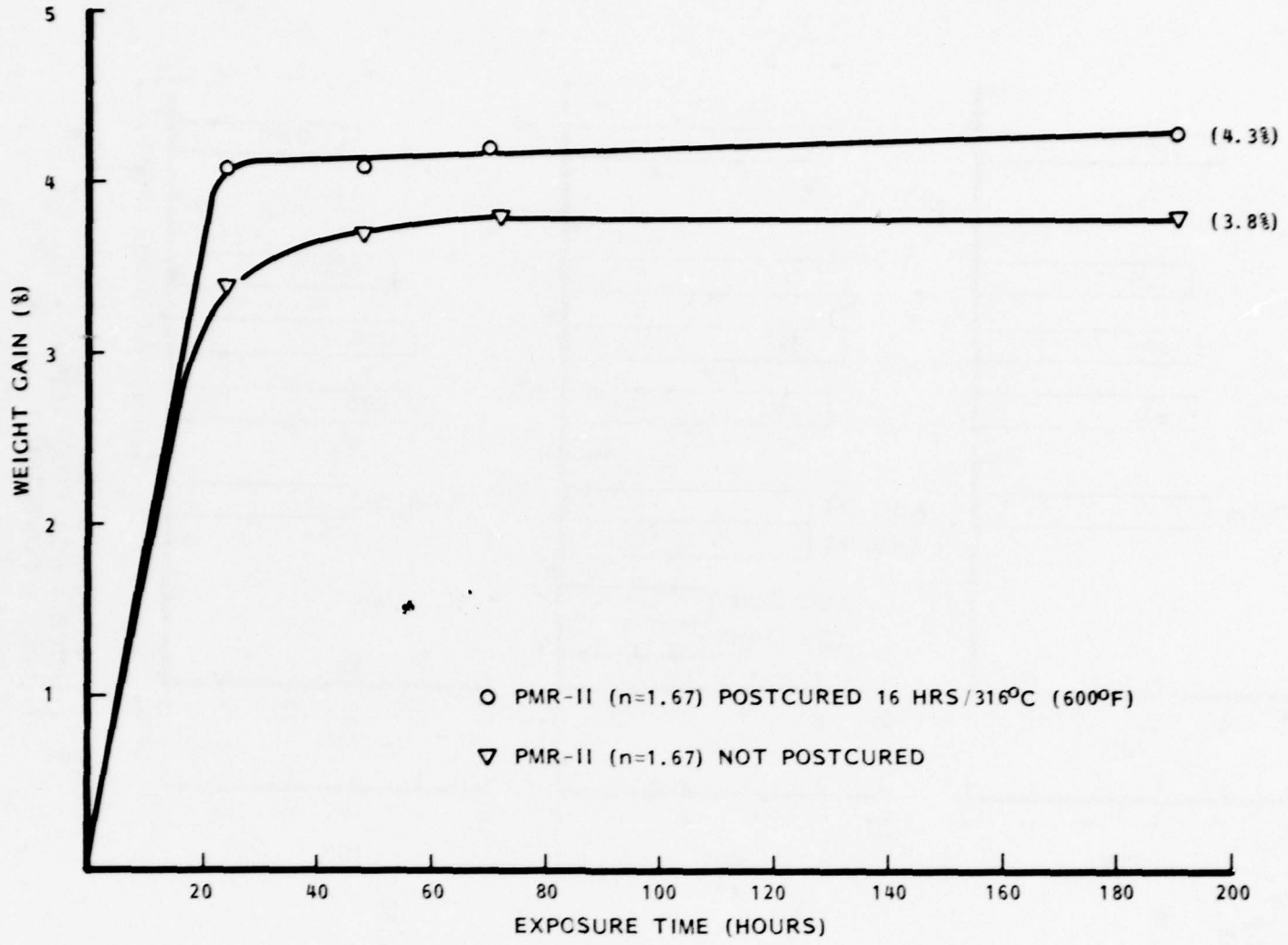


FIGURE 16 PERCENT WEIGHT GAIN OF PMR-II NEAT RESIN MOLDINGS EXPOSED TO 97% RH AT 65°C (150°F).

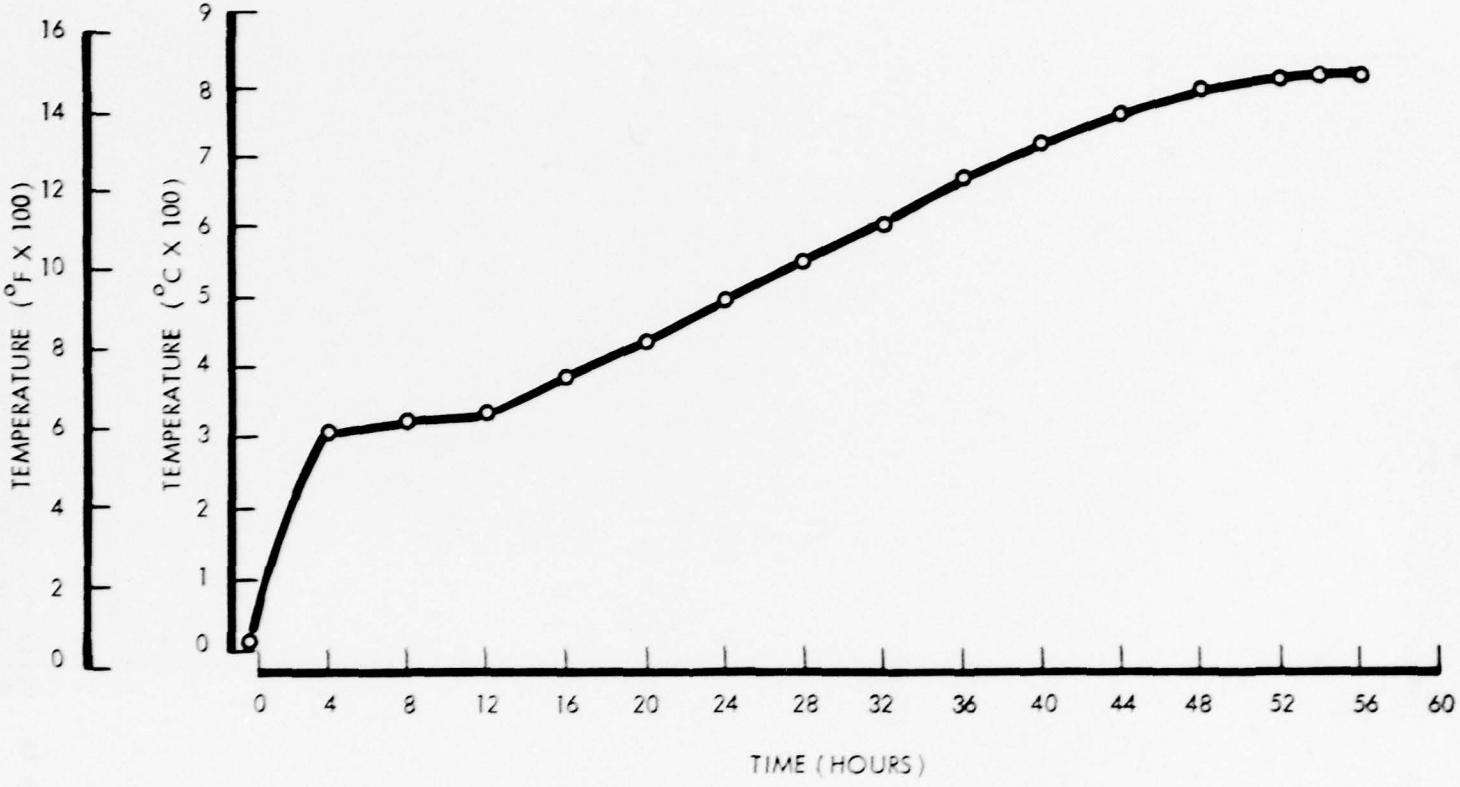


Figure 17. Temperature Cycle Used to Char Neat Resins.



Figure 18. Ultrasonic C-Scan of Postcured C-3000/PMR-II (N = 2.50) Molded at 6.9 MPa (1000 psi).

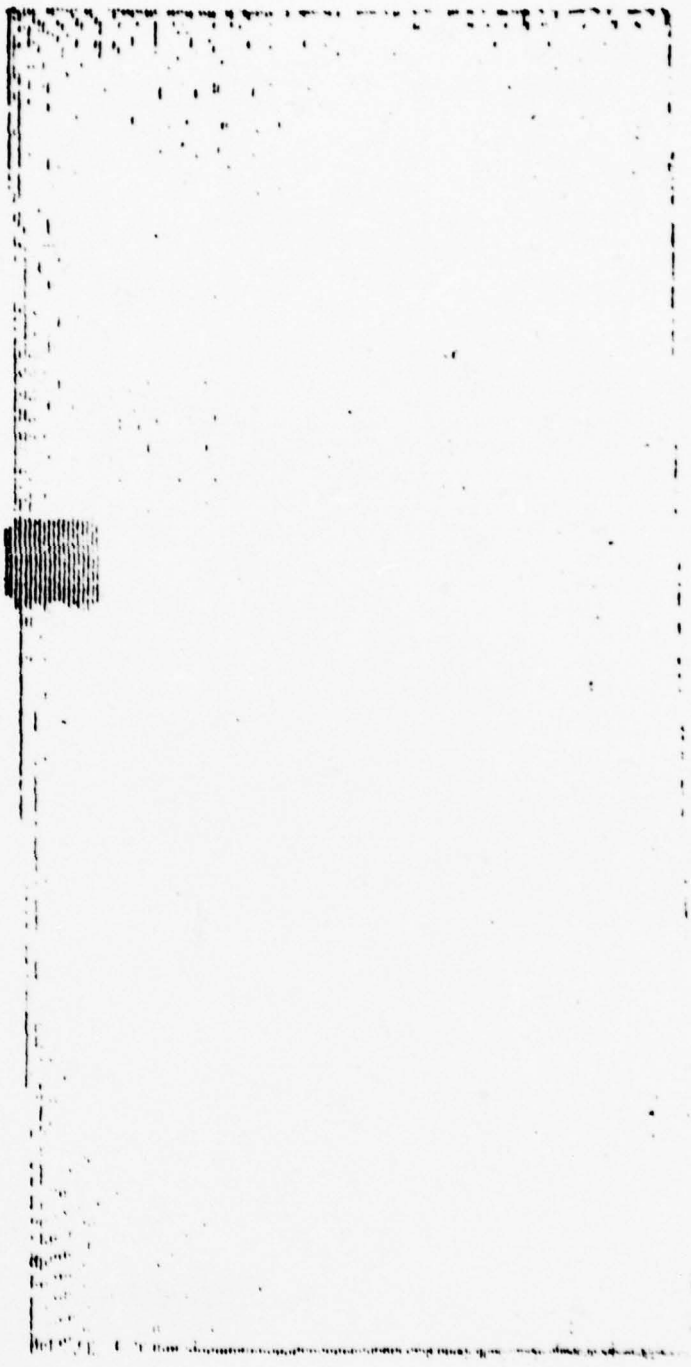


Figure 19. Ultrasonic C-Scan of Postcured C-3000/PMR-II (N = 0.167) Molded at 3.4 MPa (500 psi).



Figure 20. Ultrasonic C-scan of 21.6 x 21.6 cm (8.5 x 8.5 inch) NR-059X/C-3000 Cloth Laminate 881-66 Molded with NR-059X in the As-received Condition. (Reduced)



Figure 21. Ultrasonic C-scan of 21.6 x 21.6 cm (8.5 x 8.5 inch) NR-059X/C-3000 Cloth Laminate 881-67 Molded with NR-059X in the As-received Condition. (Reduced)



Figure 22. Ultrasonic C-scan of 10.8 x 20.3 (4 x 8 inch) NR-059X/C-3000 Cloth Laminate 881-70 Molded with NR-059X after One Week Storage at -18°C.

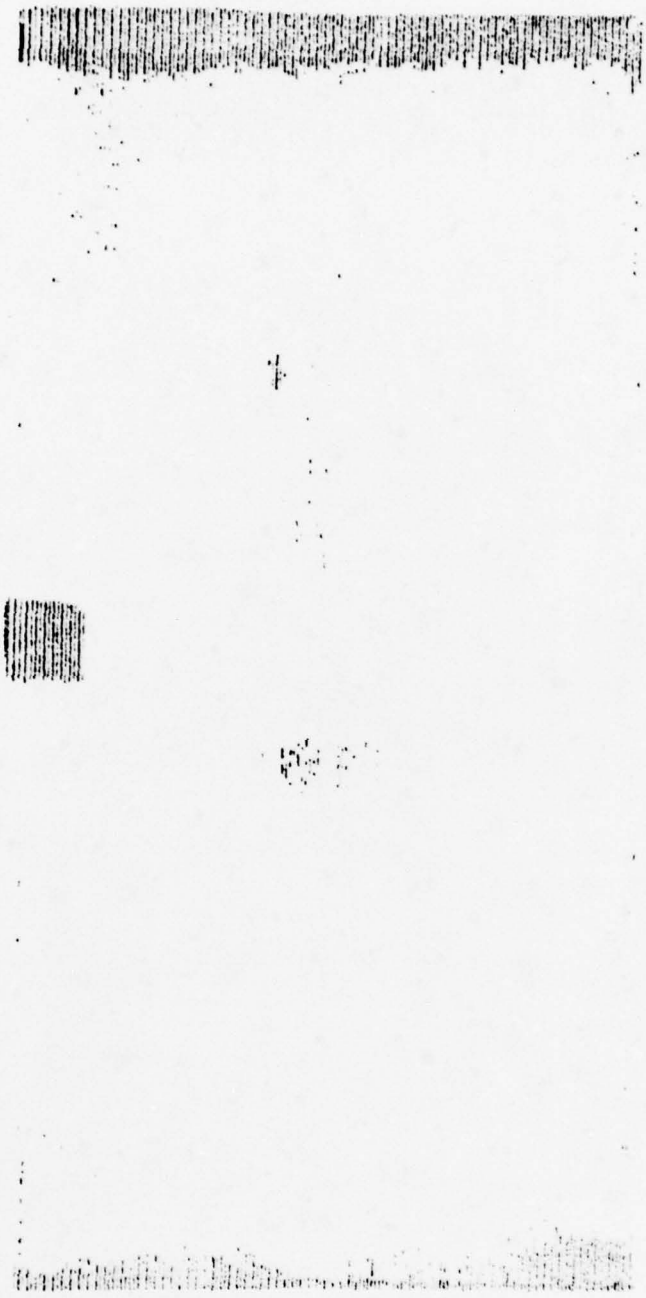


Figure 23. Ultrasonic C-scan of 10.8 x 20.3 cm (4 x 8 inch) NR-059X/C-3000 Cloth Laminate 881-73 Molded with NR-059X after Two Weeks Storage at -18°C.



Figure 24. Ultrasonic C-scan of 10.8 x 20.3 cm (4 x 8 inch) NR-059X/C-3000 Cloth Laminate 881-75 Molded with NR-059X after Three Weeks Storage at -18°C.



Figure 25. Ultrasonic C-scan of 10.8 x 20.3 cm (4 x 8 inch) NR-059X/C-3000 Cloth Laminate 881-77 Molded with NR-059X after Four Weeks Storage at -18°C.

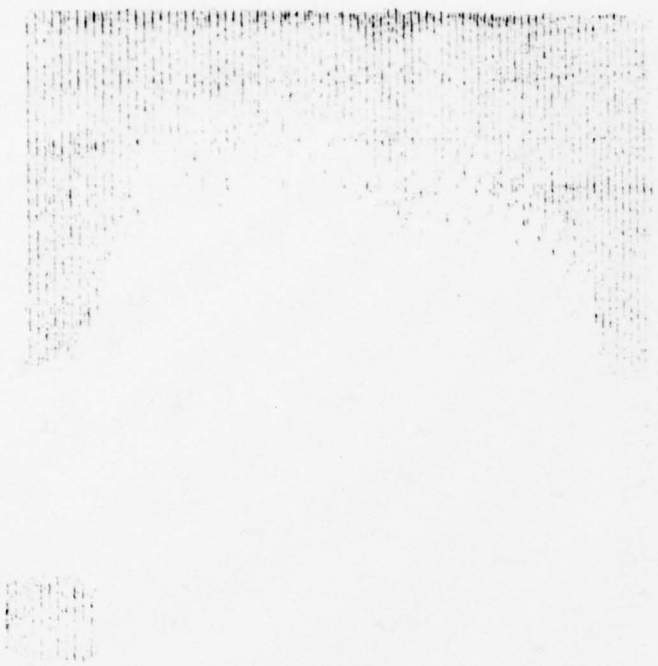


Figure 26. Ultrasonic C-scan of 10.8 x 20.3 cm (4 x 8 inch) NR-059X/C-3000 Cloth Laminate 881-79 Molded with NR-059X after Five Weeks Storage at -18°C.



Figure 27. Ultrasonic C-scan of 21.6 x 21.6 cm (8.5 x 8.5 inch) PMR-II (n = 1.67)/C-3000 Cloth Laminate 881-53. (Reduced)



Figure 28. ITGA Specimens in Chamber Prior to Closing and Installation in Oven.

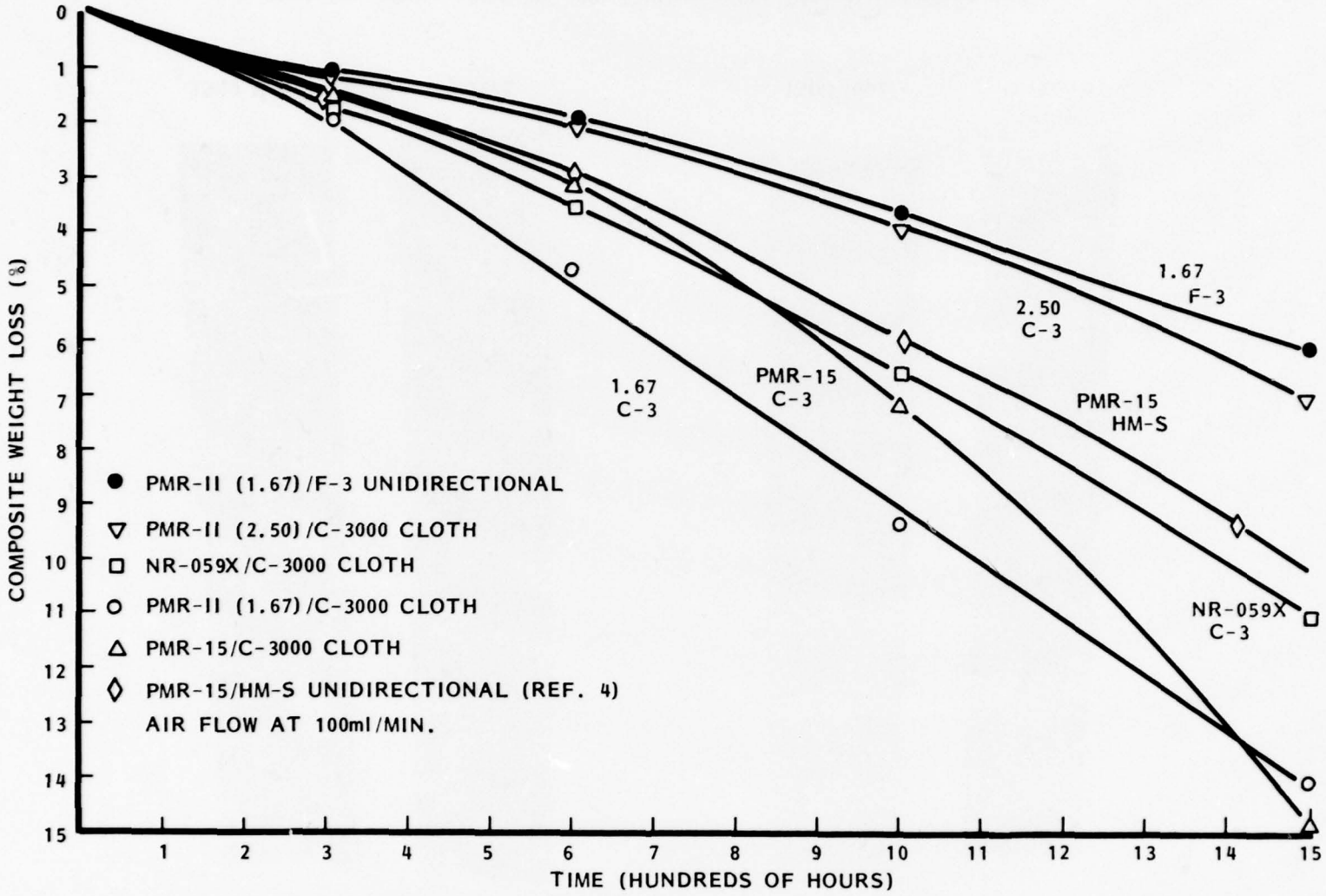


FIGURE 29 WEIGHT LOSS OF PMR COMPOSITES EXPOSED TO 316°C (600°F)

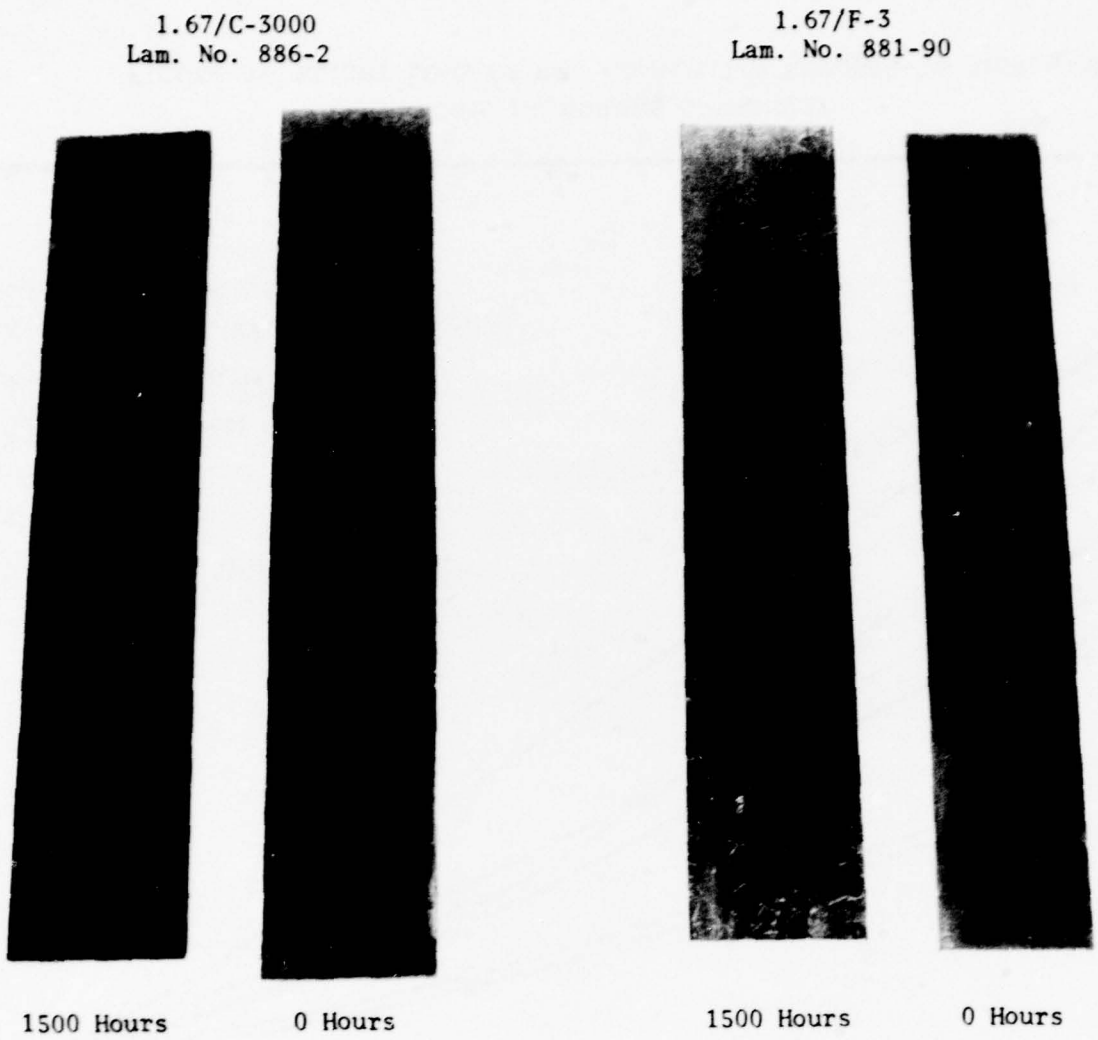


Figure 30. Comparison of PMR-II Composite Plaçques Before and After 1500 Hour ITGA at 316°C (600°F).

n = 2.50
Lam. No. 881-84

n = 1.67
Lam. No. 886-3

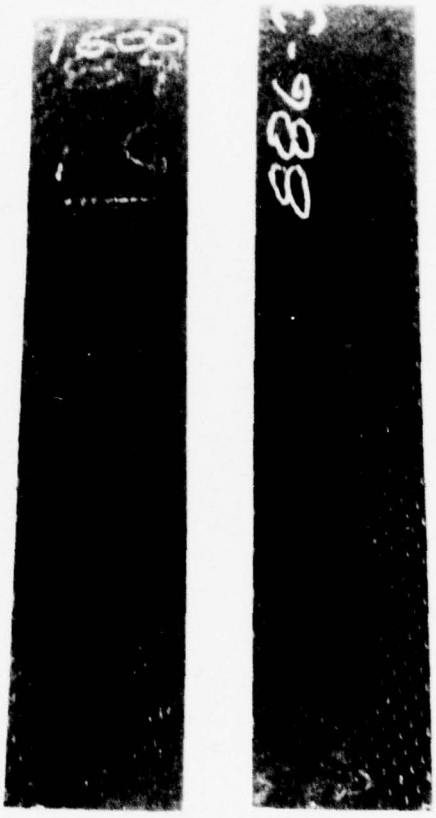


Figure 31. Comparison of C-3000 Cloth Laminates with Two FMW Levels of PMR-II After 1500 Hour ITGA at 316°C (600°F).

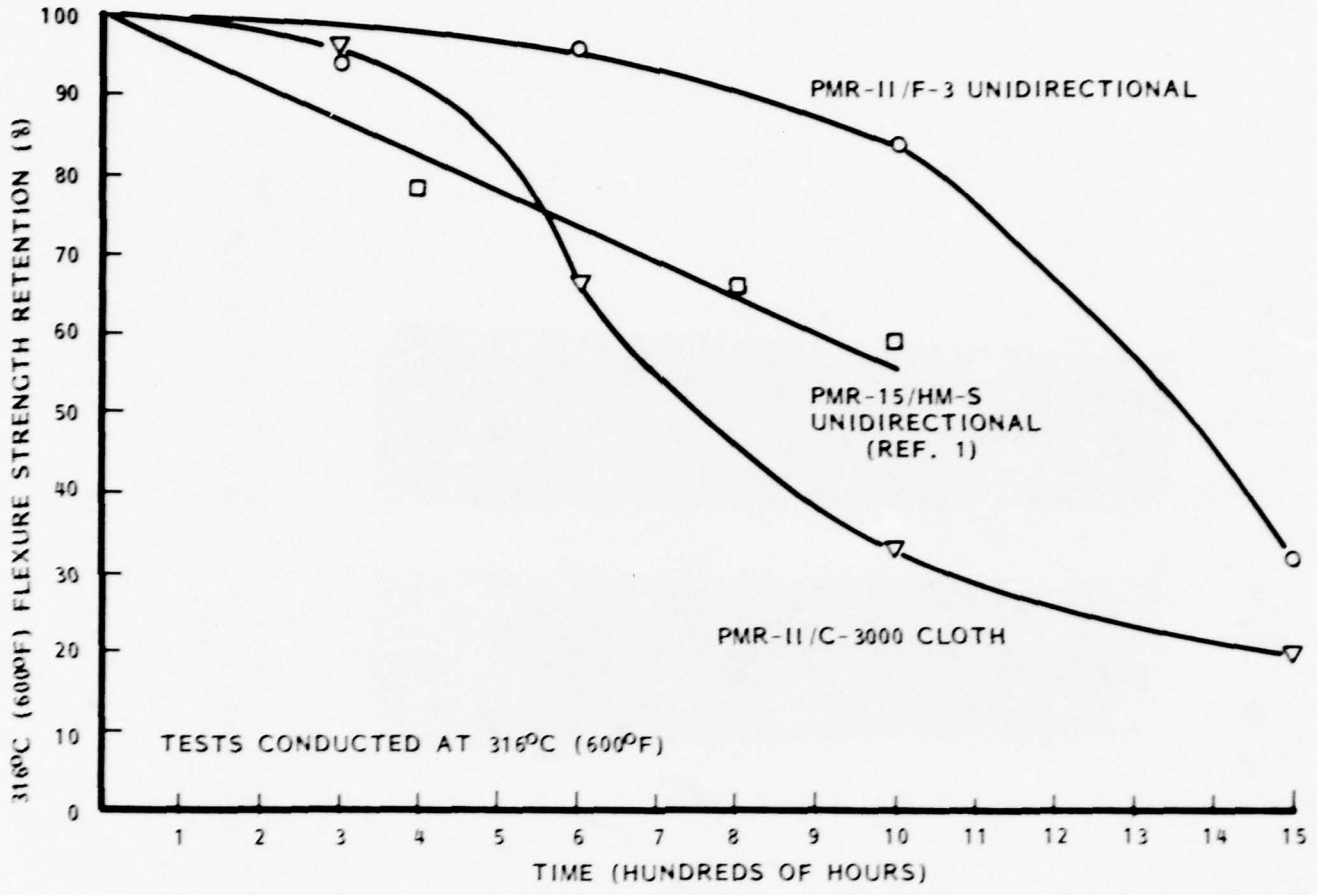


FIGURE 32 COMPOSITE FLEXURE STRENGTH RETENTION WITH TIME AT 316°C (600°F).

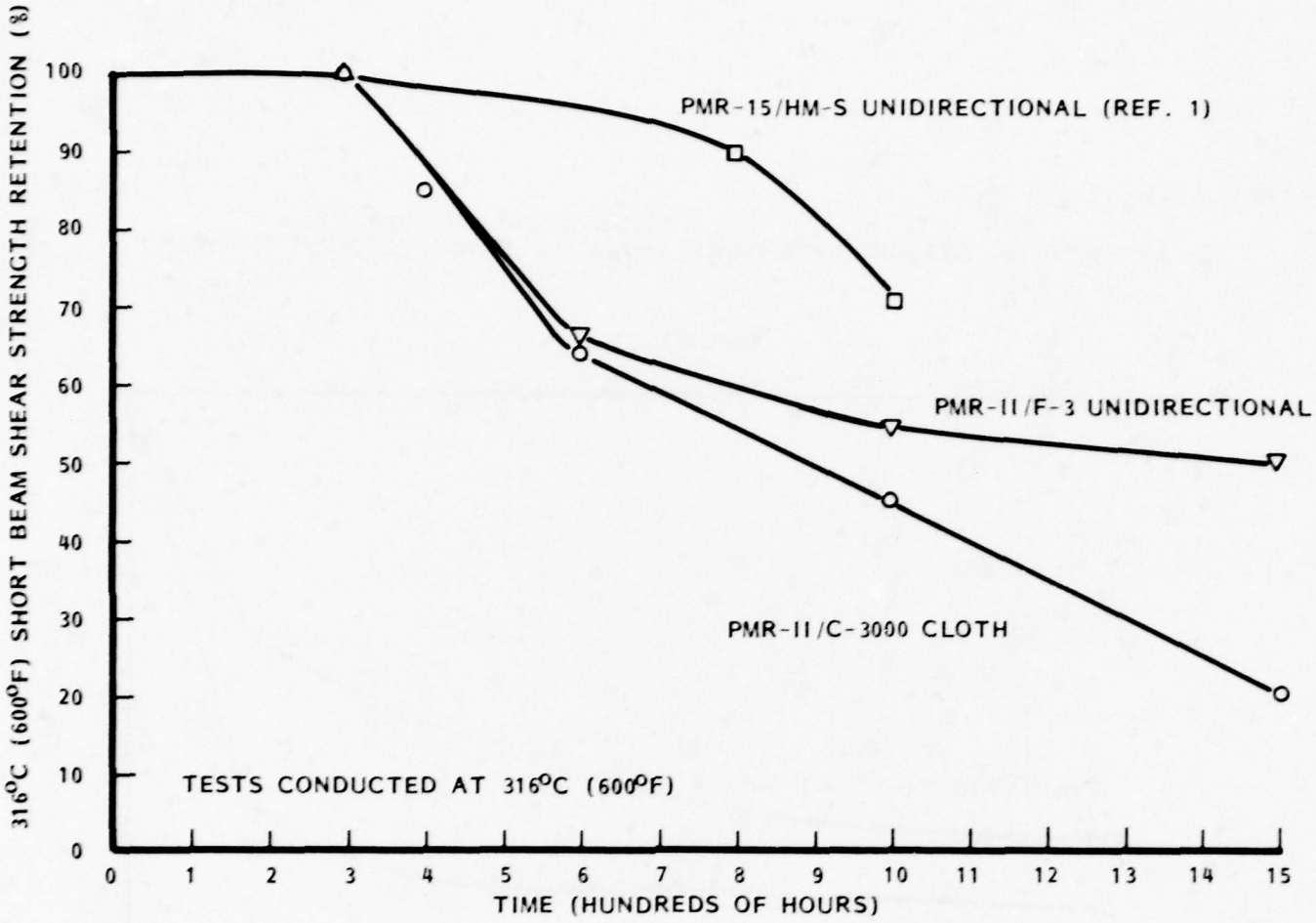


FIGURE 33 PMR COMPOSITE SHORT BEAM SHEAR STRENGTH RETENTION WITH TIME AT 316°C (600°F).

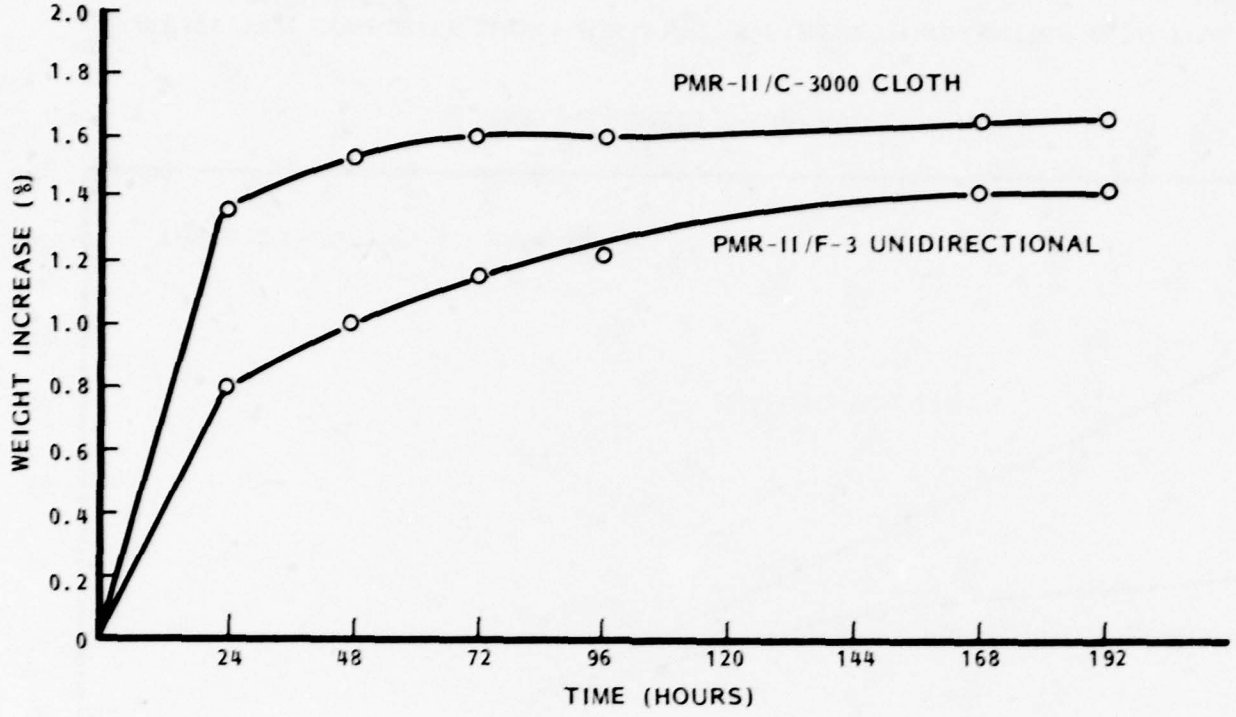


FIGURE 34 WEIGHT CHANGE OF PMR-II COMPOSITES EXPOSED TO 97% RELATIVE HUMIDITY AT 65°C (150°F).

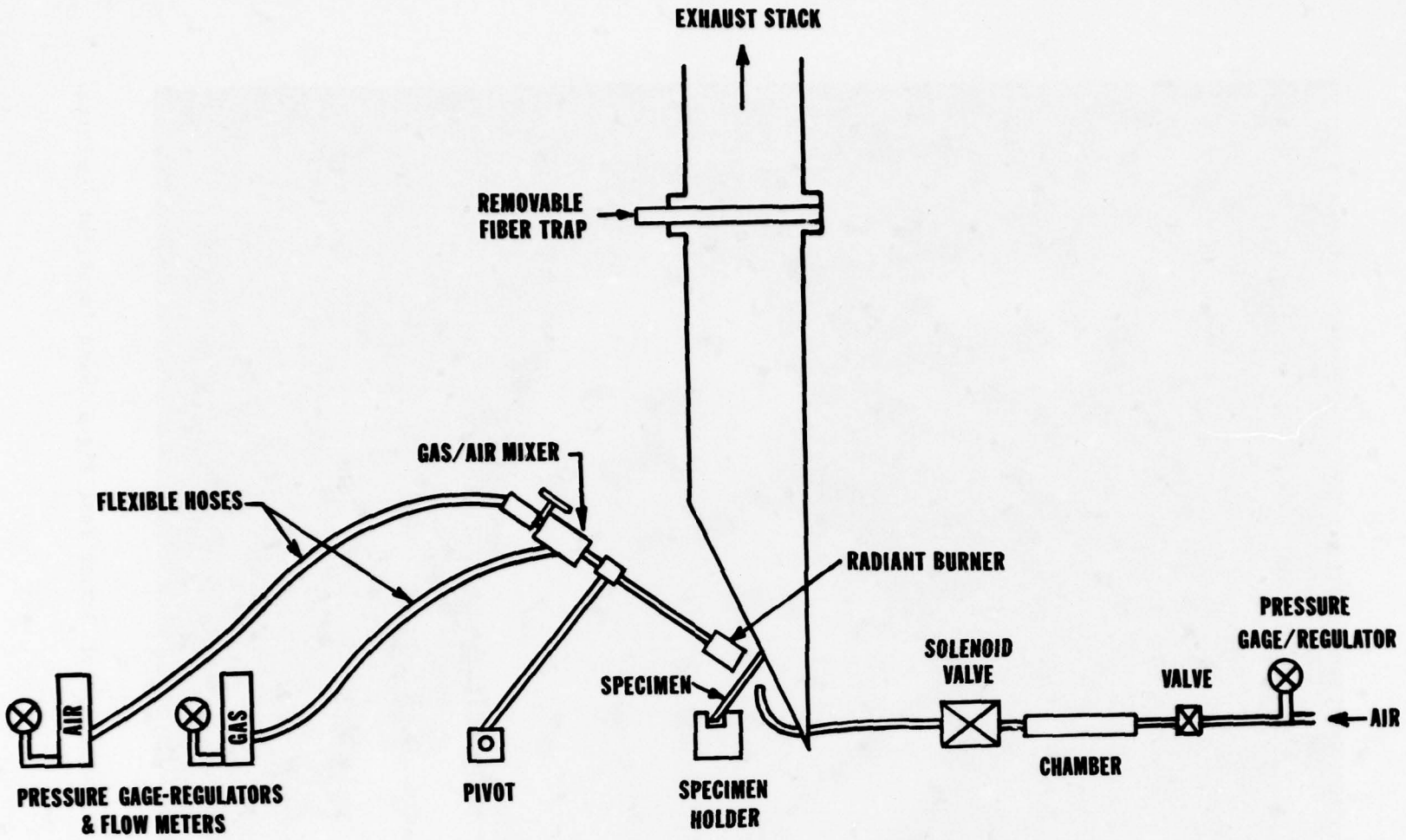


Figure 35. Burner Rig for Fiber Release Characterization.



Figure 36. Photograph of Burner Test Rig Showing Important Features.



Epoxy-Novolac PMR-II PMR-15

Figure 37. Specimens of C-3000 Cloth Reinforced Composite After Fire Test.

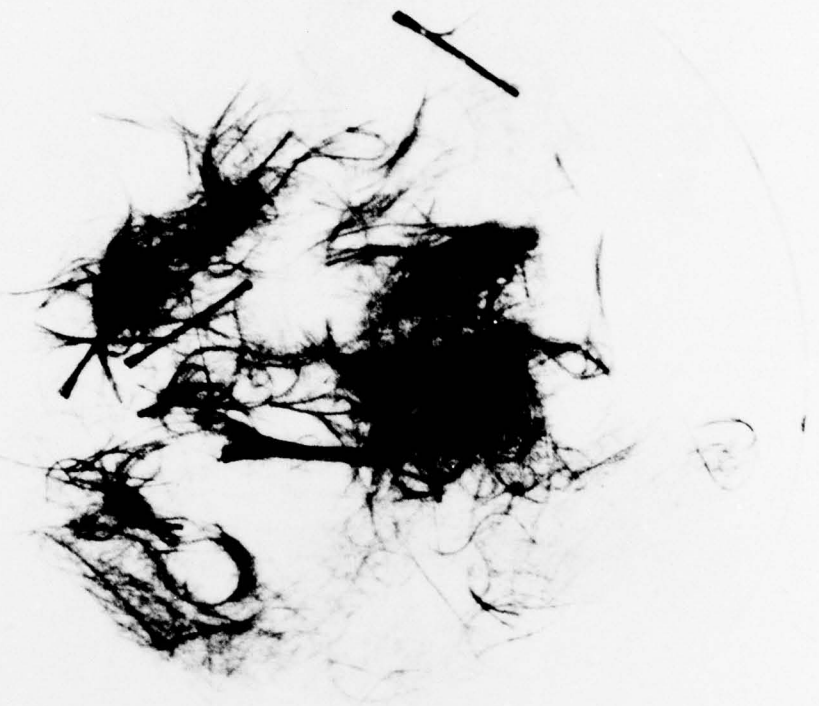


Figure 38. Fiber Debris Collected from Fire Test of Epoxy-Novolac/C-3000 Composite.

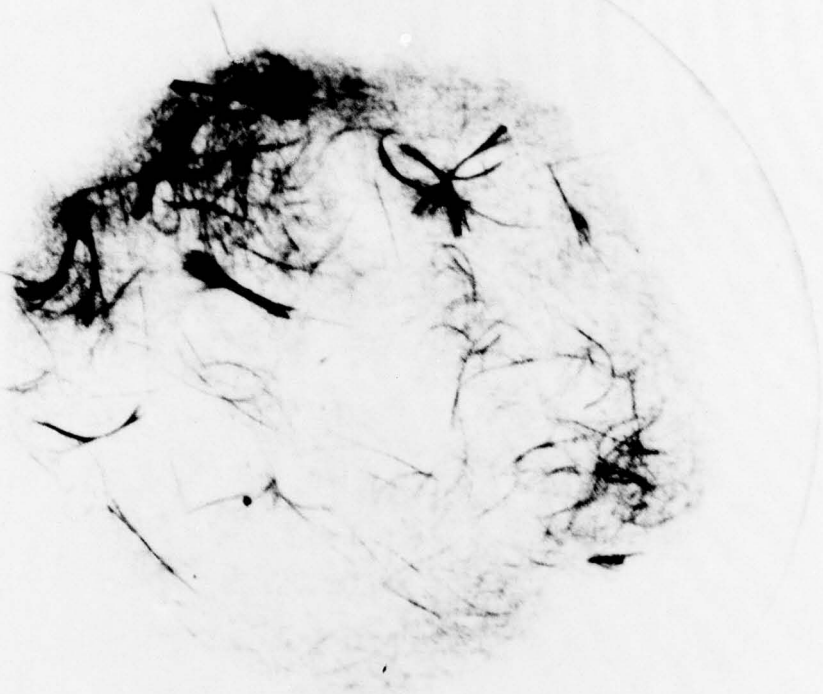


Figure 39. Fiber Debris Collected from Fire Test of PMR-II/C-3000 Composite.



Figure 40. Fiber Debris Collected from Fire Test of PMR-15/C-3000 Composite.

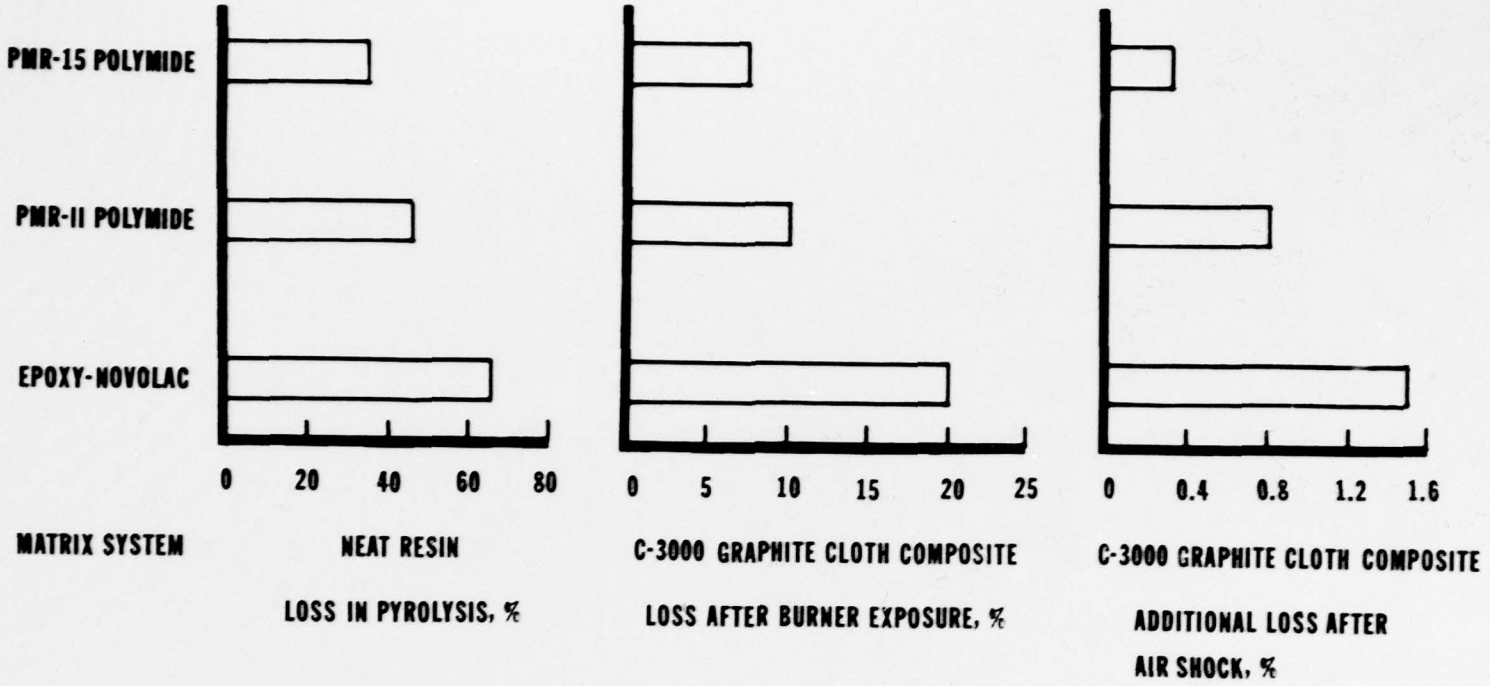


Figure 41. Incineration Characteristics of Various Matrix/Composite Systems.

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