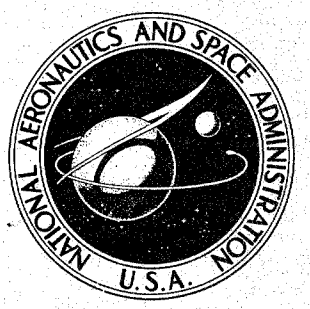
NASA CONTRACTOR REPORT



NASA CR-1723

NASA CR-1723

STUDY AND PRODUCTION OF POLYBENZIMIDAZOLE BILLETS, LAMINATES, AND CYLINDERS

by Burton S. Marks, Lester E. Shoff, and Gazel W. Watsey

Prepared by
LOCKHEED MISSILES & SPACE COMPANY
Palo Alto, Calif. 94304
for Ames Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1971

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA CR-1723		

4. Title and Subtitle	5. Report Date
Study and Production of Polybenzimidazole Billets, Laminates, and Cylinders	May 1971
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Burton S. Marks, Lester E. Shoff and Gazel W. Watsey	
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
Palo Alto Research Laboratories Lockheed Missiles & Space Co. Palo Alto, California	NAS 2-5521
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Contractor Report
National Aeronautics & Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Polybenzimidazole syntactic foam composites and polybenzimidazole-carbon cloth laminates have been produced for evaluation as ablative thermal protection systems for the proposed Space Shuttle vehicle and Planetary Probes,respectively. Processess were developed for producing these composites with consistent properties. The foam composites have densities of 0.4-0.5 gm/cm^3, have low thermal conductivity, are non-flammable, non-smoking, have low weight loss to 600°C and retain their high mechanical properties to 350°C. These PBI foam composites could also find applications as thermal and fire barriers and as cryogenic insulation.

The PBI-carbon cloth laminates have a density of 1.4 gm/cm^3 and possess high mechanical properties.

Processes are described for producing billets and cylinders of the foam composites and laminates of the PBI-carbon cloth. Physical, chemical and thermal tests were performed to characterize these composite systems.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polymeric Composites, high temperature; ablative materials; polybenzimidazoles; high temperature composites; thermal protection systems	UNCLASSIFIED-UNLIMITED

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
UNCLASSIFIED	UNCLASSIFED	158	$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

FOREWORD

This is a final report on the work covered between 25 June 1969 and 30 Sept. 1970. The work performed under Contract No. NAS 2-5521, entitled "Study and Production of Polybenzimidazole Laminates, Billets, and Cylinders".

The National Aeronautics and Space Administration technical monitors were Mr. Demetrius Kourtides and Mr. Ernest L. Winkler under the technical direction of Dr. John A. Parker; all of the Ames Research Center, Moffett Field, Calif.

At Lockheed Missiles & Space Company, Palo Alto Laboratories, Dr. B. Marks managed the program with Mr. L. E. Shoff and Mr. G. W. Watsey carrying out the experimental, processing, and fabrication procedures. Mr. A. Ozolin ably assisted in the testing and sample preparation.

PROGRAM SUMMARY

The Lockheed Missiles & Space Company, under Contract with the National Aeronautics & Space Administration, Ames Research Center, has developed new processing methods and techniques for the fabrication of the following items:

1. Low density 30 lb/ft^3 polybenzimidazole composite billets
2. Low density 30 lb/ft^3 polybenzimidazole composite cylinders
3. High density (1.35-1.40) polybenzimidazole-carbon cloth laminates.

The techniques and processing developed are reproducible and have been repeated a minimum of ten times for items 2 and 3 and twenty-seven times of item one. Specifications covering the processing and manufacturing standards for all three items are included in this report.

The processing methods are sufficiently versatile to allow for various shape and density changes as may be required.

The program included a material study of the components used to prepare these composite structures; polybenzimidazole resin, phenolic microballoons, glassy carbon microballoons, chopped carbon fibers and effects of fiber length, carbon cloth fabrics. Extensive testing of the component materials, as well as the completed structure was carried out.

The composite structures were delivered to NASA-Ames Research Center for further mechanical testing, filling with transpiration coolant for items 1 and 2, and ablation testing of all items. At Ames Research Center, excellent ablation test results were obtained with filled and unfilled item 1 and 2 composite structures. Some of the results are discussed in the conclusion.

CONTENTS

LIST OF TABLES AND FIGURES

Section 1

INTRODUCTION AND OBJECTIVES

This report outlines the work effort in support of NASA's program for superior ablative heat shields required for certain space missions. It deals with the fabrication of high performance polybenzimidazole ablative heat shields of two types:

A. Low density syntactic foam type billets and hollow cylinders

B. Carbon cloth high density laminates.

These composite materials with their superior ablative properties should be useful in the following areas:

1. Inexpensive replaceable heat shields for reentry of a reusable space vehicle from earth orbit
2. Aft-body section and heat shield of Venus probe
3. Airplane brake lining
4. Preparation after pyrolysis of reusable transpiration type heat shields
5. Preparation of carbon foams.

It is the purpose of this program to duplicate the results reported in the literature[1,2] and attempt to better these results based on Lockheed's experiences with polybenzimidazole resins[2,3] and Lockheed's new glassy

carbon microballoons .

In essence, Lockheed will prepare billets, laminates, and cylinders; study of some of their physical properties; work out fabrication problems and prepare specification and manufacturing standards to cover these composites. NASA will take the delivered items and test them physically and ablatively for use in the areas listed above.

Section 2

BACKGROUND

2.1 LOW DENSITY PBI COMPOSITES

In the literature[1] low density .5 gm/cc char forming polybenzimidazole composites compounded with carbon fibers and phenolic microballoons were prepared and ablation tested. The best reported composite formulation contained[1]:

69% PBI prepolymer

13% Carbon fibers

18% Phenolic microspheres or balloons.

The composite was cured in a Teflon vacuum bag by controlled heating from 120°C - 315°C, with a post cure under Argon at 315°C - 455°C.

Ablation tests were conducted at Ames Heat Transfer Tunnel on blunt-faced models, with a nose radius of 6.12 cm and a diameter of 3.81 cm, and a thickness of 2.86 cm. The tests were in air at a nominal stagnation point surface pressure of 2.5 atm., with a nominal stream enthalpy of 9.3×10^6 J/kg.

Under these test conditions Material 5, Table 1, which had the composition shown above, gave the best test results; namely, the lowest mass loss rate of .018 gm/sec-cm^2 at the stagnation point where r/R = 0 and the lowest mass loss rate at a point r/R = .8 of .023 g/sec-cm^2. Materials 2, 3, and

4 in Table 1 were composed of 65% PBI, 15% carbon fibers, 20% phenolic microballoons. The thermally crosslinked system No. 2 shows less loss at the stagnation point than chemically crosslinked Material 3 or 4, and is approximately equivalent or better loss rate at r/R = .8. On this basis it appears the thermally crosslinked resin system containing 65% PBI gives a good overall result. In the case of Material 5, the chemically crosslinked 69% PBI system, unfortunately no thermal crosslinked system was run in comparison with it. It would seem based on the analogous 65% PBI system that equivalent or possibly better results might be obtained with a thermally crosslinked versus chemically crosslinked 69% PBI system.

The overall conclusions drawn on these ablation studies[1] were that the ablation performance of polybenzimidazole composites can be substantially improved by crosslinking. The improvement is noticeable both in the regions of high surface shear and no shear in the case of the thermally crosslinked system and some of the chemically crosslinked systems.

A study of thermally induced crosslinked polybenzimidazole (PBI) resin used to prepare carbon cloth laminates was carried out by Lockheed Missiles & Space Company[3]. In this study it was found that PBI was still thermoplastic from 750° - 850°F, and did not become thermoset until 900°- 950°F. A curing schedule and technique were developed to effect thermosetting or crosslinking. Based on this,high performance ablative laminates were obtained, which are discussed in section 2.2.

TABLE 1

ABLATION PERFORMANCE OF PBI MATERIALS[1]

Mat'l	Type	gm/cc	V_s r/R=0 cm/sec.	V_s r/R=0 gm/sec.cm^2	V_s r/r=0.8 gm/sec.cm^2	Char Appearance
1	Linear	0.480	0.053	0.025	0.047	Rough surface with pits
2	Thermally cross-linked	0.550	0.037	0.020	0.026	Rough surface
3	Chemically cross-linked (oxidation of 3,3' - diamino-benzidine)	0.496	0.053	0.026	0.025	Slightly rough surface with small pits
4	Chemically cross-linked (triphenyl trimeasate)	0.416	0.094	0.039	0.051	Very irregular surface with deep fissures
5	Chemically cross-linked (oxidation of 3,3' - diamino-benzidine)	0.048	0.041	0.018	0.023	Smooth surface
6	Phenolic nylon	0.545	0.061	0.033	0.060	Slightly rough surface

2.2 COMPOSITIONS

Based on the above studies, it was the intent of this work to prepare a low density PBI composite of the following composition:

PBI	- 69%
Carbon Fibers	- 13%
Phenolic Microballoons	- 18%

Commercially available polybenzimidazole resin was to be used and would be thermally crosslinked using conditions and techniques discussed above.(3) In a similar vein, to upgrade the composition, the phenolic microballoons will be replaced with glassy carbon microballoons. The glassy carbon microballoons have the following added advantages over their phenolic counterparts:

- o do not contain oxygen bearing functional groups to interact with the char and cause internal oxidation.
- o show superior ablation properties in that they do not decompose at lower temperatures, break up, and form gaps in the composite structure as experienced by the phenolic microballoons. Indeed, glassy carbon shows oxidation resistance comparable to pyrolytic graphite as seen in Figure 1.
- o should aid in char formation.

The glassy carbon microballoons should give similar density control to that obtained with the phenolic microballoons.

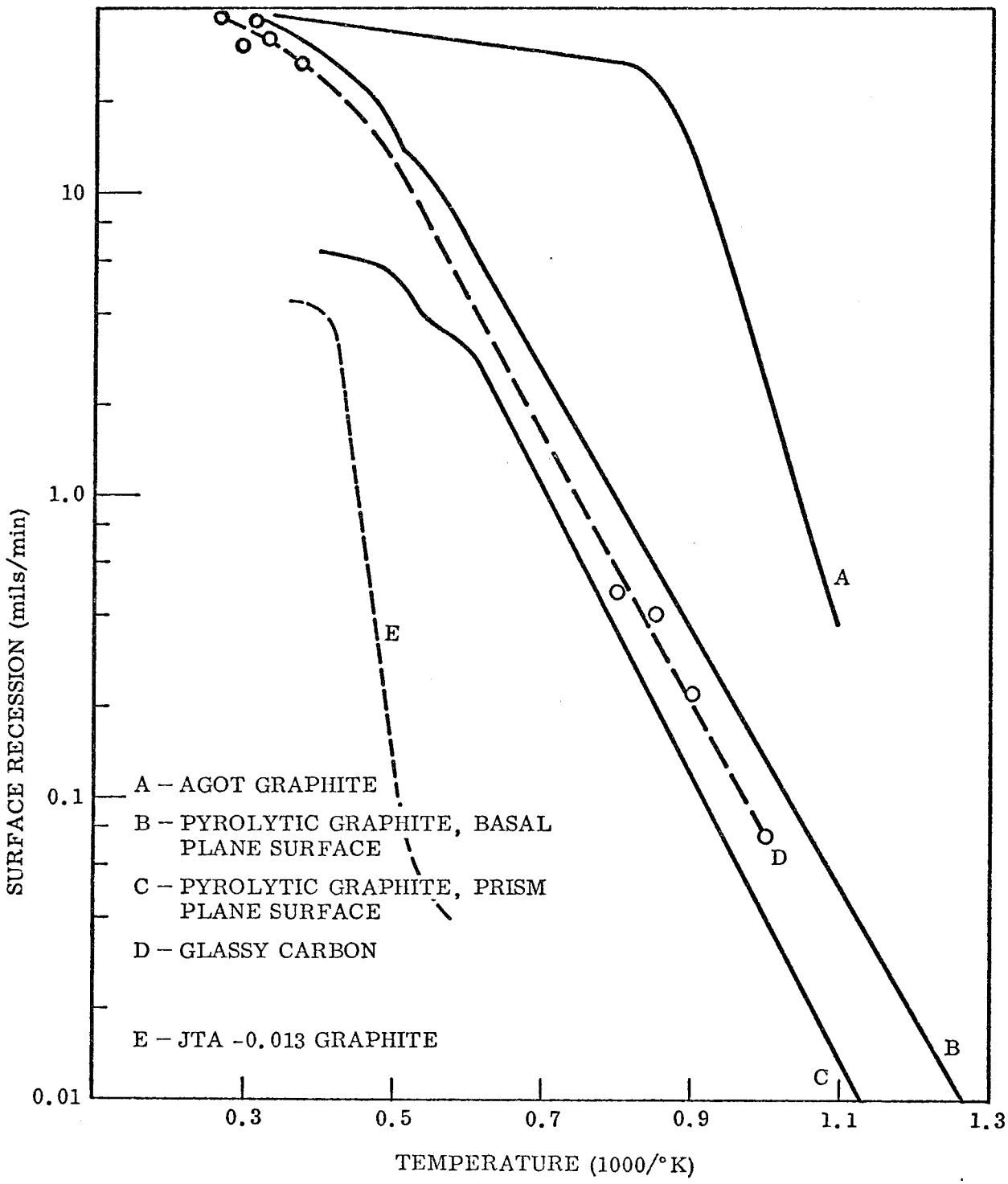
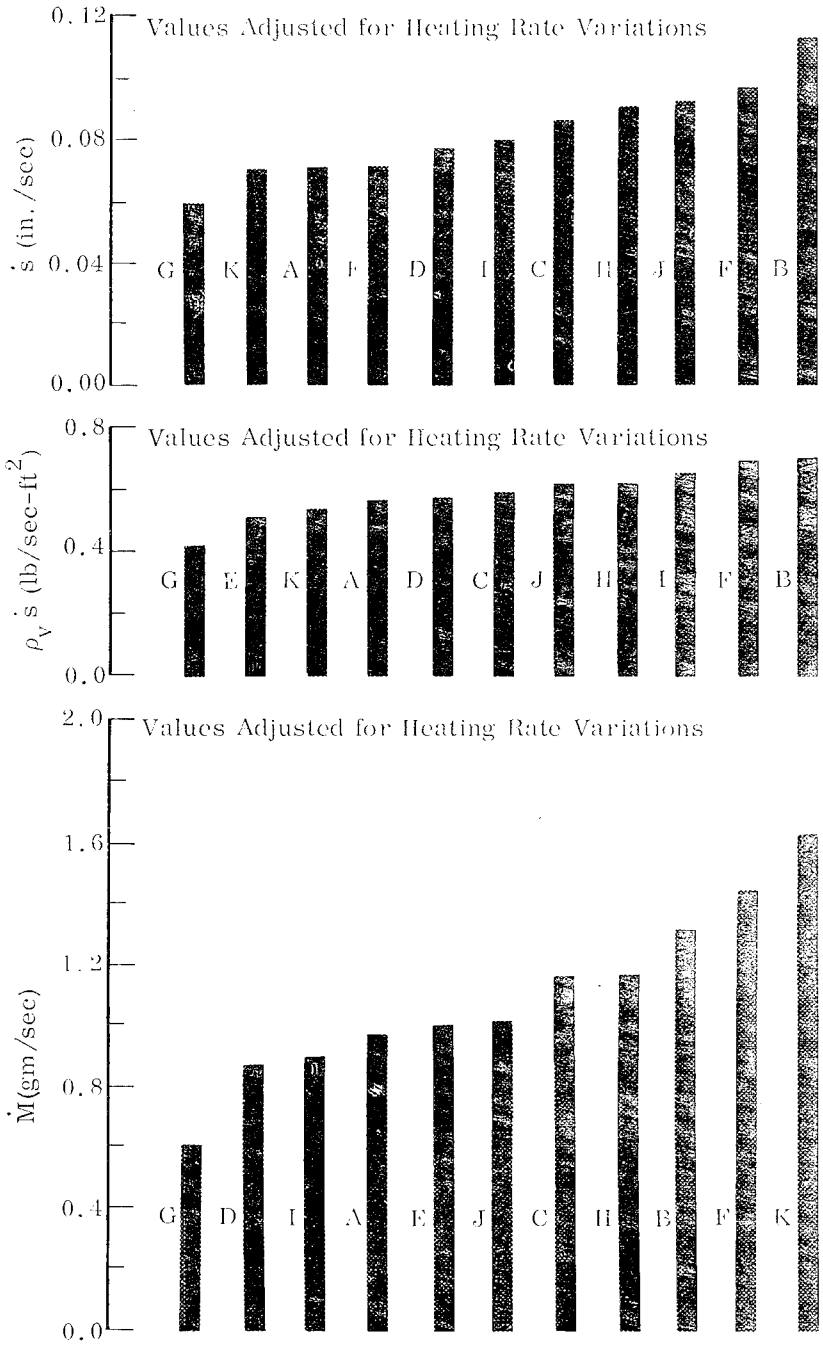


Fig. 1 Oxidation Resistance of Glassy Carbon in Free Convective Air as Compared With Graphite



A - Phenol-Formaldehyde
B - 2,7-Napthalenediol-Phenol-Formaldehyde
C - o,o'-Biphenol-Formaldehyde
D - p-Phenylphenol-Phenol-Formaldehyde
E - 2,7-Napthalenediol-o,o'-Biphenol-Formaldehyde
F - Polyimide
G - Polybenzimidazole
H - Polyphenylene Oxide Copolymer
I - Polybenzothiazole
J - Polyphenylene (Branched)
K - Polyamide-Imide

Fig. 2 Quantitative Ablation Results, Resin Composites, and Laminates

Table II

ABLATION PERFORMANCE OF PBI LAMINATES

Operating Variables			Material Designation	Pretest Material Properties			Gross Test Results			Measured Erosion		
Mass Flow Rate Lb/sec.	Chamber Pressure BTU/lb. Atm	Stagnation Enthalpy BTU/lb. Atm	Laminate	Percent Resin	Virgin Density lb/ft.	Barcol Hardness	Total Wt. Loss (gm)	Max. Surface Erosion (in)	Surface Temp. °R	Max Erosion Rate (in/sec)	Max. Mass Loss Rate Lb/ft^2-sec.	Total Mass Loss Rate /sec.
.207	25.7	4010	Polybenzimidazole-Pluton B1 - Laminate prepared by Narmco	48.4	66.2	63	.953	.111	5350	.104	.590	.89
.207	25.7	4010	Polybenzimidazole-Pluton B-1 - Laminate prepared by LMSC using special processing technique	44.6	84.4	98	.535	.054	5180	.057	.401	.56

Table III

RESINS CHOSEN FOR COMPARISON

Resin Type	Supplier
A. Phenol-formaldehyde	Monsanto (SC-1008)
B. 2,7-Napthalenediol-phenol-formaldehyde	Hughes
C. o,o'-Biphenol-phenol-formaldehyde	Evercoat Chemical
D. p-Phenylphenol-phenol-formaldehyde	Ironsides (DP-25-10)
E. 2,7-Napthalenediol-o,o'-biphenol-formaldehyde	Evercoat Chemical
F. Polyimide	Dupont (PI-4701)
G. Polybenzimidazole	Narmco (Imidite 2801)
H. Polyphenylene oxide copolymer (2,6 dimethyl and 2-methyl-6-allyl)	Rocketdyne
I. Polybenzothiazole	Abex Corp.
J. Polyphenylene (branched)	Hughes (Abchar 412B)
K. Polyamide-imide	Amaco (AI-11)

Table IV

QUALITATIVE RANKING SUMMARY

Rate[a] + Fabric[b]	Ablation Test Data				Mechanical Data	TGA Data	
	Maximum Erosion Rate, $\dot{S}$ (in./sec)	Mass Rate $\rho_V \dot{S}$ (lb/ft^3-sec)	Total Mass Loss Rate, $\dot{M}$ (gm/sec)	Char Form Rate	Four-Point Flexural	10% Loss	1000°C Weight Loss
A. Phenol formaldehyde (SC-1008)	3	4	4	5	1	9	8
B. 2,7-Napthalenediol-phenol-formaldehyde	11	11	9	7	10	11	7
C. o,o'-Biphenol-formaldehyde	7	6	7	4	3	10	3
D. p-Phenylphenol-phenol-formaldehyde	5	5	2	2	2	7	9
E. 2,7-Napthalenediol-o,o'-biphenol-formaldehyde	4	2	5	8	5	6	6
F. Polyimide (PI-4701)	10	10	10	11	8	3	10
G. Polybenzimidazole (Imidite 2801)	1	1	1	6	4	1	2
H. Polyphenylene oxide copolymer	8	8	8	3	9	8	11
I. Polybenzothiazole	6	9	3	9	7	2	5
J. Polyphenylene (branched) (Abchar 412)	9	7	6	10	11	4	1
K. Polyamide-imide (AI-11)	2	3	11	1	6	5	4

(a) Resin content 39 to 44% of laminate.
(b) Fabric used in each case was Pluton B-1 (3 M Co.).

In consequence, the alternate heat shield compositions decided upon was:

PBI	- 69%
Carbon Fibers	- 13%
Glassy Carbon Microballoons	- 18%

2.3 POLYBENZIMIDAZOLE CARBON CLOTH LAMINATES

A study of thermally induced crosslinked polybenzimidazole (PBI) resin used to prepare carbon cloth laminates was carried out by Lockheed Missiles & Space Co.[3] In this study it was found that PBI was thermoplastic at 750-850°F and did not become thermoset until 900-950°F. A curing schedule and technique were developed to effect thermosetting or crosslinking. Based on this procedure, high performance ablative laminates were obtained, as shown by the second example in Table II, which is compared to first example laminate produced by Narmco (resin manufacturer and formulator). The Narmco example was reported by them to be thermoset, although other evidence indicates the contrary.[3] The ablation results and erosion in Table II show that the new curing schedule and technique, indeed, produce a thermoset resin which is greatly superior to the non-thermoset resin.

A comparison of the thermoset PBI resin with other newer commercially available or near commercially available resins used in ablation was carried out at Lockheed Missiles & Space Company.[2] The resin systems used and the sources of supply and qualitative ranking are shown in Tables III and IV. Of particular interest was the fact that the thermoset PBI was first in all ablation testing. Figure 2 quantitatively shows these ablation results.

This ablation testing was carried out at the Arnold Engineering Development Center's five megawatt Air Arc Heater, under conditions of 4-10 atm. sample surface pressure, 5000-10,000 BTU/ft^2 sec. sample surface heat flux. The stream at the nozzle had an enthalpy of 4,500 BTU/lb. with an arc chamber pressure of 26 atm. These ablation tests were carried out on wedge shape specimens.(2)

Section 3

BILLETS AND CYLINDERS

3.1 COMPONENT MATERIALS STUDIES

The billet and cylinder composition required, as considered in the previous section, the following composition by weight:

69% Polybenzimidazole

13% Carbon Fibers

18% Phenolic or Glassy Carbon Microballoons

3.1.1 Component Materials Properties

The designation, supplier, and specification for these raw materials are as follows:

Polybenzimidazole (PBI) "Imidite 2801" - Whittaker Corporation

a.	Density	Spg: 1.28 - 1.32
b.	Polymer Melt Temperature	115°C to 130°C
c.	Particle Size	50 Mesh, 90% 50-200 Mesh
d.	Weight loss (500°F cured PBI)	20% ± 2.0%
e.	Insolubility of PBI in (hot) H_2SO_4 after post cure	98% ± 1.0%

Carbon Fibers "CCA-1" - Hitco Corporation

a.	Composition	95% amorphous carbon min.
b.	Fiber length	1/2" Nominal
c.	Volatile Content	3.0% max.

Phenolic Microballoons - BJO-0930, Union Carbide Corporation

a.	Bulk Density	0.10 - 0.12 g/cc
b.	True Density	.322 - .334 g/cc
c.	Particle Size	20 mesh, 90% 50-100 mesh
d.	Broken Balloons	3%
e.	Volatile Content	8.0% max.

Glassy Carbon Spheres - LMSC Glassy Carbon Grade 1000, Lockheed Missiles & Space Company

a.	Bulk Density	.135 -.165 g/cc
b.	True Density	.358 -.370 g/cc
c.	Particle Size	20 mesh, 90% 50-100 mesh
d.	Broken Balloons	3%
e.	Volatile Content	3.0% max.

It should be noted that the above specifications are part of the "Specifications and Manufacturing Standard" shown in Appendix "A".

For brevity's sake the methods of determining these above physical properties will not be fully covered in the text, however, they are satisfactorily covered in Appendix "A", the "Specification and Manufacturing

Standard for the PBI Billets".

During the program certain areas of difficulty and interest relative to the raw materials were encountered and these are discussed.

3.1.2 Weight Loss of Component Materials on Curing

It was decided to begin the work by first learning of the weight loss of the individual components following the curing temperatures required for the billets. This was required so that the load or batch size for loading the preform mold could be determined in order to obtain the required density of the composite.

Each of the materials, Hitco, CCA-1 carbon fiber, Phenolic Microballoons BJO 0930, and the Polybenzimidazole Imidite 2801, were run separately through the recommended curing and post-curing schedule up to 850°F and 950°F respectively in a Lindberg Tube Furnace. The method involved weighing each specimen in a graphite or quartz dish, which was then loaded in the furnace. The ends of tubes were sealed and dry nitrogen purged through the tube during the cycle and continued after until the temperature was below 300°F. The major volatilization from the PBI resin occurred at 600°F-650°F.

The following weight loss was noted on these runs:

Materials	Temp. Range	% Wt. Loss	Temp. Range	% Wt. Loss
Carbon Fibers	R.T. to 850°F	-	R.T. to 950°F	1.9%
Phenolic Microballoons	R.T. to 850°F	36.9	R.T. to 950°F	41.9%
PBI - Resin	R.T. to 850°F	27.4	R.T. to 950°F	31.3%

No attempt was made to precondition the specimens; in consequence, the carbon fiber and phenolic microballoons contained water vapor. Preconditioning both of these at 300°F/1 hr showed that the carbon fiber contained 1.4% water vapor and the phenolic microballoons contained 7.2% of water vapor, etc.

If one does not precondition the component material, then a billet prepared from 69% PBI, 13% carbon fibers, 18% phenolic microballoons will theoretically lose 30.6% by weight after post cure to 950°F.

It must be remembered that the 30.6% will be the upper limit of weight loss in that the individual material in this test had a large surface area and heating was relatively rapid, as compared to billet curing.

It should be noted that the phenolic microballoons BJO 0930 lose 7.2% by weight at 300°F/1 hr. These are, however, preconditioned by pressurization to 60 psi to burst weak-walled balloons. The balloons are then sieved through a 35 mesh screen, followed by flotation in toluene. The floating balloons, approximately 80% of the original, are removed and air dried.

These phenolic microballoons have no broken balloons and have a bulk density of .109 g/cc. They lose up to 36.9% volatiles at 850°F. Their particle size is 100% < 100 mesh. The volatile content is 7.7% at 300°F after 1 hour. This last value is greater than the 3% value set forth in the contract specification. To correct this the microballoons were heated at 300°F/2 hours, pressurized to 60 psi, and floated in toluene to remove sinkers. Just prior to use, the balloons are dried for 1 hr. at 300°F.

As a result, the bulk density of the phenolic microballoons are increased to 0.114 g/cc and the true density is 0.329 g/cc.

These phenolic microballoons appear to be further cured by the preconditioning as was noted in lower weight loss on curing in following tests. The tests were conducted on phenolic microballoons and carbon fibers which were preconditioned by heating to 300°F/1 hour to insure drying or reduction of volatiles and stored in a desiccator. This preconditioning is standard before the components are used in billet or cylinder fabrication.

Two specimens of each component were weighed into preweighed ceramic dishes. The specimens were then placed into a nitrogen atmosphere controlled furnace. Temperature was run rapidly to 500°F, followed by further heating to 950°F, through the cure and post-cure schedules used to prepare billets.

The specimens were cooled in the furnace to 250°F, then removed to a desiccator for further cooling before reweighing. The results of these tests show the following weight losses:

	Carbon Fibers	
Specimen	No. 1	No. 2
Weight of Specimen	8.0211	7.9800
Wt. Loss	.0975	.1338
% Wt. Loss	1.22	1.68

Specimen	Phenolic Microballoons No. 1	No. 2
Weight of Specimen	5.5555	5.5865
Wt. Loss	1.2335	1.4021
% Wt. Loss	22.2	24.7

3.1.3 Comparison Studies of Polybenzimidazole Batches

Difficulties were encountered in preparing billets using one of the batches of Imidite 2801 (Polybenzimidazole). For this reason a more detailed comparison examination of the two resin batches was undertaken, since these batches were used to prepare the billets and cylinders.

3.1.3.1 Melting Point

A Fisher-Johns melting point apparatus was used for this determination. The same operator determined all melting points which were carried out at the same time.

	Lot 92 1st Shipment	Lot 92 2nd Shipment	Lot 93
Found:	115-118°C	114-117°C	112-115°C
Reported by Whittaker Corporation:	124°C		125°C

The melting points are somewhat subjective, although an attempt was made to make the test as objective as possible. Our results would not correlate with the Narmco-Whittaker test results. A telephone call to their production control lab in Costa Mesa informed us that their melting point report is the point of complete fluidity.

3.1.3.2 Weight Loss Determination on Curing

Samples of Batch 92, 1st and 2nd shipments, and Batch 93 were weighed into preconditional (dried), preweighed, ceramic vessels and heated to 500°F in air following the billet curing cycle (see Table V). They then were cooled and weighed and showed excellent precision in weight loss between samples of the same batch.

After this the individual samples were ground to a 30-mesh powder and reweighed into preconditional (fired), preweighed, ceramic vessels. These samples were heated in an inert atmosphere (dry N_2) rapidly to 500°F whereupon the curing and post curing schedule for the billet was followed. After cooling down to room temperature the weight loss was determined.

	1st Shipment Batch 92 % Weight Loss		2nd Shipment Batch 92 % Weight Loss				Batch 93 % Weight Loss	
RT-500°F	20.7%	20.7%	21.2%	20.8%	21.3%	21.3%	20.1%	20.0%
500-950°F	12.2%	11.1%	10.4%	9.9%	10.4%	9.4%	8.7%	9.6%
RT-950°F	32.9%	31.8%	31.6%	30.7%	31.7%	30.7%	28.8%	29.6%
Avg.	32.4%		31.2%				29.2%	

The results indicate that Batch 93 has less volatiles lost than either shipment of Batch 92. The two shipments of Batch 92 also show differences of 1.2%. It would appear, however, that Batch 93 loses 2 to 3% less volatiles than Batch 92, and this was computed in subsequent billet preparation and fabrication.

Based on these results it would appear that Batch 93 is further advanced than Batch 92.

3.1.3.3 Melt-Index

Utilizing a Tinius Olsen Extrusion Plastometer (Melt Indexer) the melt-index of Batch 92 (lst shipment) and Batch 93 were obtained. The method used in this test is given in Instruction Booklet No. 63-11A by the Tinius Olsen Testing Co., Willow Grove, Pa.

The course setting of 583 and a fine setting of 200 resulted in a temperature in the plastometer of 120.0°C. Both batches were run at this setting with the following average of 2 runs:

Batch 92 - 1.0560 gms/1 min.

Batch 93 - .6128 gms/1 min.

Since the accepted expression for melt index is g/10 minutes, the following represents the results:

Batch 92 - 10.56 g/10 min.

Batch 93 - 6.12 g/10 min.

It is quite apparent that Batch 93 is further advanced than Batch 92, which is in keeping with results in the last section.

It should be noted that this test is subjective in that it is very dependent on the operator. Extreme care in repetition of the steps and procedures was required to obtain reproducible results.

3.1.3.4 Solubility of Post-Cured Resin in Hot Concentrated H_2SO_4

Comparative hot sulphuric acid solubility tests were run on polybenzimidazole Batch # 92 and Batch # 93. The following technique was developed and applied to carry out this test:

1. PBI resin (Batches 92 and 93) was cured and post-cured under identical conditions as were employed in the preparation of the billets.
2. The cured resin was ground to a 20-30 mesh size, dried one hour at 300°F, cooled in a desiccator, and 1.5 to 3.0 g weighed into capped containers.
3. Fifty cc of concentrated sulphuric acid was added to each weighed specimen and heated to 100°C, held for one hour, and then cooled to room temperature.
4. The mixture was filtered through tared fritted glass filters.
5. The contents of each filter were then flushed four times with an addition of 50 cc. concentrated H_2SO_4 to remove all traces of dissolved resin, and then washed with 200-250 cc of water until filtrate is neutral.
6. The tared fritted glass filter and resin was dried at 300°F/3 hrs, cooled in a desiccator and weighed to determine weight of insoluble resin.

The following results were obtained:

Batch Specimen	Batch 92 # 1	Batch 92 # 2	Batch 93 # 1	Batch 93 # 2
% Soluble Resin	.96	.71	1.07	.87
% Insoluble Resin	99.04	99.29	98.93	99.13

It seems apparent that the cured resin of either Batch 92 or 93 are similar

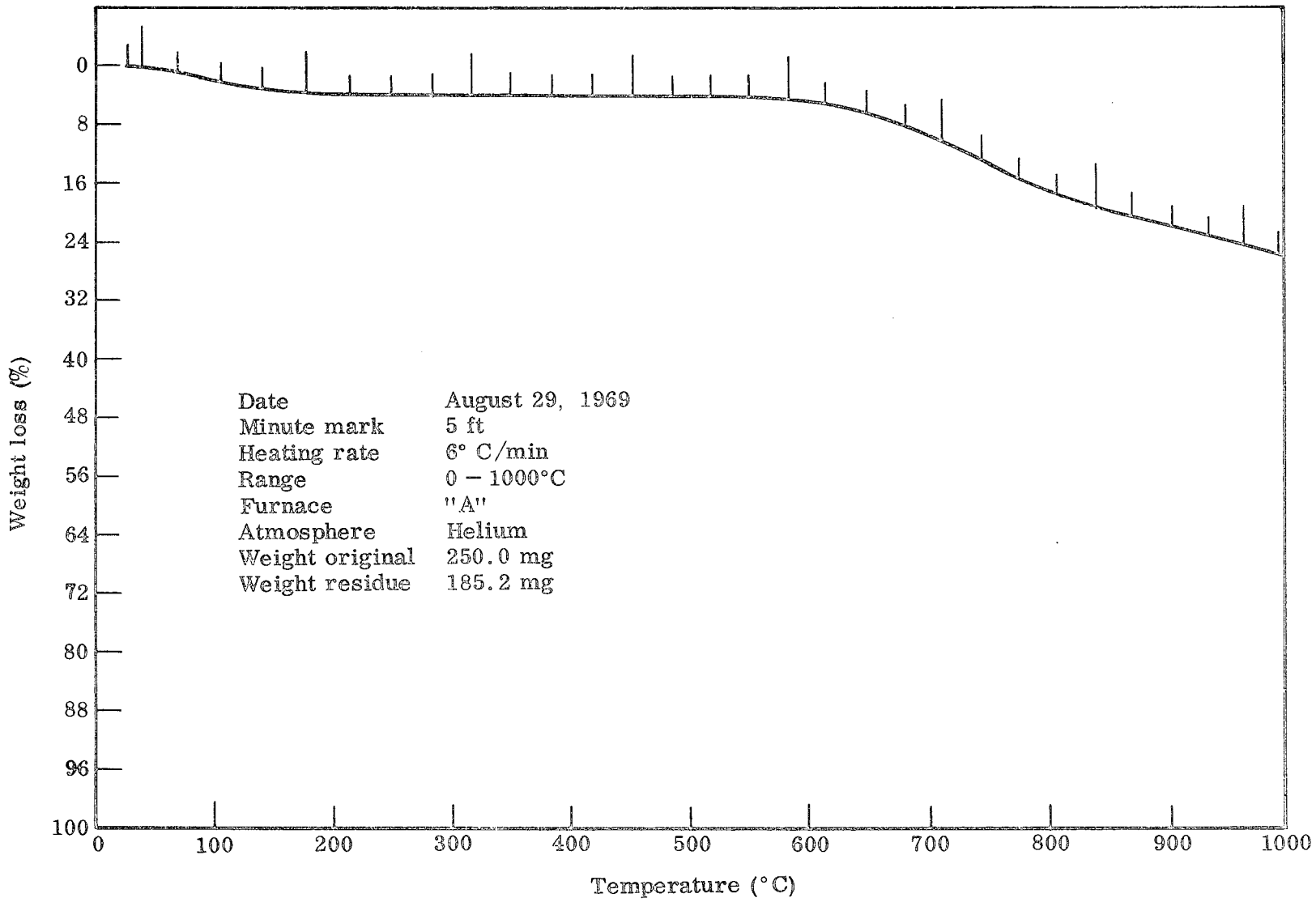


Fig. 3 Thermogravimetric Analysis of PBI Resin Batch No. 92

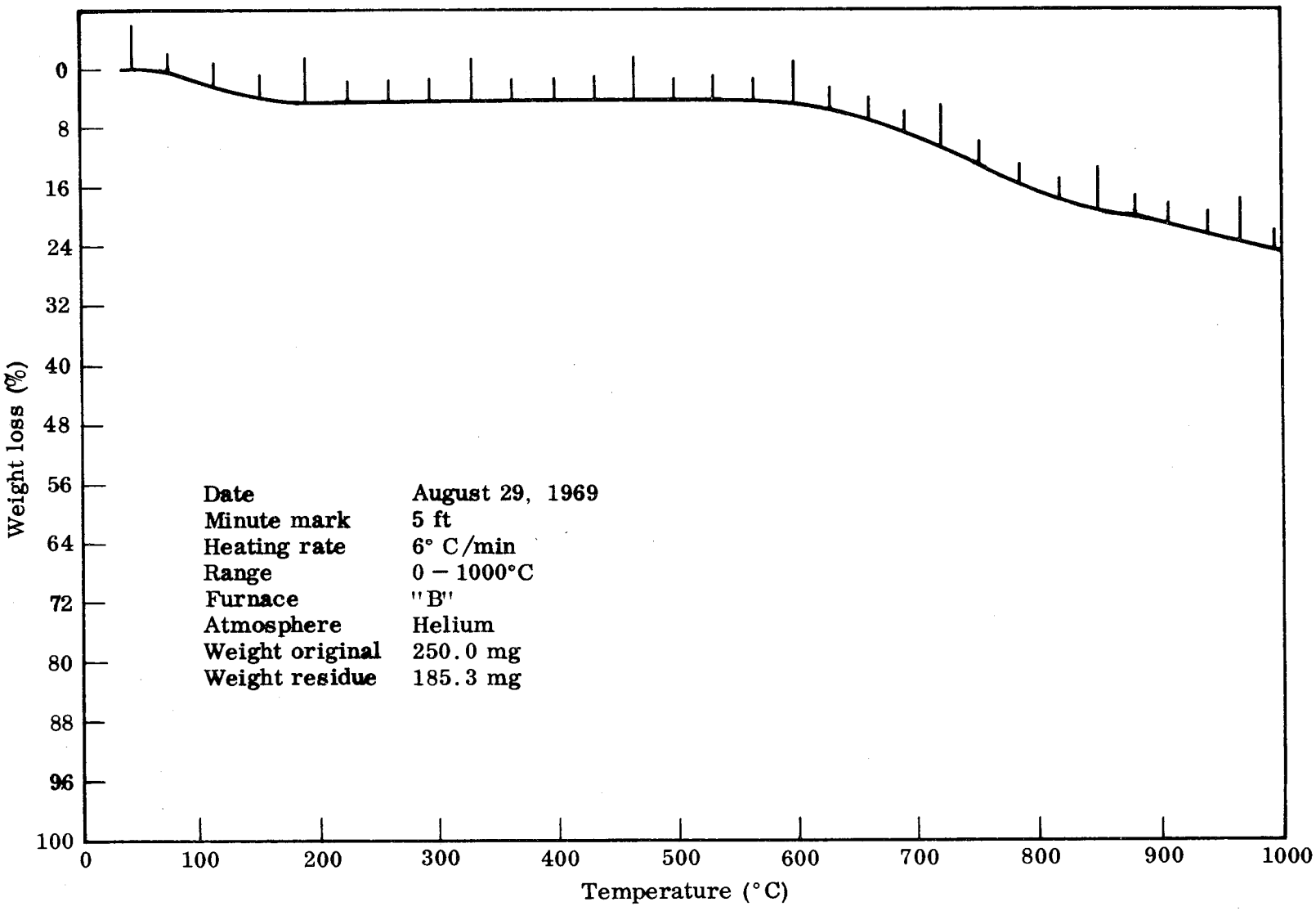


Fig. 4 Thermogravimetric Analysis of PBI Resin Batch No. 93

in their low solubility $<$ 1% in conc. H_2SO_4.

In essence, one can conclude that the crosslinking densities of postcured resin of either batch are equivalent.

3.1.3.5 Thermogravimetric Analysis

Thermogravimetric analysis of the cured resin from Batch 92 and Batch 93 Imidite 2801 was also carried out. These are shown in Fig. 3 and Fig. 4. The resins were cured under the typical cure conditions of time and temperature used to prepare the billets (see Table V, section 3.2.1). Vacuum curing to 600°F was replaced by curing of the batch resin in a dry nitrogen atmosphere. Both the batches lost 21.12% and 21.08% respectively by weight at 1000°C, which indicates the great similarity between the two batches.

3.1.4 Carbon Fiber Length Studies

Carbon fiber, 1/2" lengths which were precut by the manufacturer, are a 13% by weight and 5% by volume component of the billets and hollow cylinders. During the component or V-blending mixing operation a fuzzing of the fiber ends resulted in fiber becoming entangled in each other and resulted in the formation of an agglomeration of fiber balls. This gave a general undesirable inhomogeneity in the cured billets and hollow cylinders. To alleviate this, as discussed later in this report, the fibers were hammer-milled with the resin and sieved. This resulted in a homogeneous billet with a material reduction in the fiber size to 1/64" - 3/64" as well as some thickness reduction. It was felt that longer fibers, randomly and homogeneously dispersed in billet should increase ablative stability, and increase tensile

and impact strength of the composite. To correct this problem, carbon fibers of 1/4-1/2" lengths with non-fuzzing ends were prepared and compounded into composites in the following manner.

CV2-1, single ply carbon yarn from H. I. Thompson Co. was impregnated with a 10% solution of polybenzimidazole (Imidite 2801) in an equal mixture of furfural and furfuryl alcohol. Impregnation and initial B-Staging was carried out simultaneously. The B-stage curing tunnel being at 300-350°F to volatilize the solvent. After the initial impregnation and B-Staging the yarn was processed through the impregnation resin solution for the second time and again followed by B-Staging through the curing tunnel.

The yarn was wound on a take-up drum and further B-Stages through a cure schedule up to 500°F, where it was held for 30 minutes, and then allowed to cool. The carbon fibers appeared to be well impregnated, with sufficient concentration of PBI. Resin content was determined and calculations showed 20-21% pickup.

The impregnated yarn was chopped to a nominal 1/4" fiber length, using a Model 24 LB Sleeving Cutter (MacDonald & Co.). The ends were solid, and chipping and fuzzing were at a minimum.

A composite was made up consisting of the following:

12.5% Impregnated fiber (20% resin - 80% fiber)
3.0% Milled carbon fiber
66.5% Polybenzimidazole Resin
18% Glassy Carbon Microballoons

Mixing was accomplished in a V-Blender mixing the impregnated fibers with the glassy carbon beads first for approximately 10 minutes, followed by the addition of the PBI and carbon fiber mix, which was previously mixed in the V-Blender for 10 minutes with the PBI, and then followed by screening through a 25-mesh screen. This entire mixture was then mixed for an additional 10 minutes. The mixture was transferred to the preform mold and hydraulically pressed to produce a billet having a density of 37.5 lb/ft^3.

The preformed billet was cured in the standard 8" x 8" x 1" billet curing mold, using the standard cure cycle (see Appendix "A"). Build-ups were used to occupy the excess area in the mold. Because of the limited amount of work in this area, and the size of the preform billet, no attempt was made to equalize the pressure header used in the curing mold. Consequently, uneven pressure was applied to the preform. Therefore, the cured billet was cut into 2 pieces and squared. Specimen No. 1 had a density of 37.1 lb/ft^3, while specimen No. 2 had a density of 38.5 lb/ft^3.

Fiber orientation and general billet homogeneity appeared to be excellent.

Under a nitrogen atmosphere, the normal post-cure schedule for billets was followed using a tube furnace. The two specimens had the following resultant densities:

Specimen No. 1 - 33.8 lb/ft^3

Specimen No. 2 - 35.3 lb/ft^3

In a similar fashion to that described above, a composite was made of the

following:

69% PBI Resin

18% Glassy Carbon Microballoons

13% Impregnated fiber (20% resin - 80% fiber)

The density of the post cured specimen was 30.0 lb/ft^3 with homogeneous fiber distribution. These three specimens were delivered to NASA-Ames for impact and notch sensitivity testing.

3.2 BILLET PREPARATION AND PROPERTIES

In section 2.1 low density polybenzimidazole composites or billets previously prepared by the NARMCO-Whittaker under NASA-Ames are discussed. The polybenzimidazole resins used therein were in the main specially prepared polybenzimidazole systems (see Table I) in which crosslinking was obtained via chemical crosslinking functional groups initially available in the monomers or chemically induced by oxidation to be available for subsequent crosslinking. The thermally crosslinked system in Table I was cured to a maximum of 850°F, which we had found to be insufficient to insure sufficient crosslinking.[3]

In comparison the resin used in all of this work in this report was not specially produced, but was the commercially available Imidite 2801 which is the low molecular weight copolymer of 3.3'-diaminobenzidine and diphenyl isophthalate. Crosslinking was obtained exclusively by thermal means. Attempts at following the "Process Specification for Polybenzimidazole Heat Shield (KKJ) 30.9-1" 10/2/67 which had previously been used to prepare these

earlier billets, met with a lack of success. For these reasons material preparation was markedly changed and new tooling techniques used. These are discussed in section 3.2.1.

3.2.1 Fabrication & Processing

The fabrication and processing procedure developed by LMSC to obtain homogeneous, reproducible billets of a given density is documented in the billet specification in Appendix "A".

As indicated in the last section utilizing NASA Specification (KK5) E-AA-H 30.9-1 developed by Narmco gave billets which did not meet the specifications. This was due to inhomogeneity introduced by fiber ballings noted on introduction of mix into preform mold. New preforming and curing schedules and composite changes had to be developed to obtain the desired density required for the finished billets. Curing with a tooling mold guaranteed flat repeatable specimens of an exact size and configuration. These changes and the reasons they were instituted are shown in Table V.

The drawings of the tooling are shown in Figs. 5-8. Figs. 5 and 6 show the preform mold for the 1" and 2" thick billets, while Fig. 7 gives the top plate assembly and Fig. 8 the bottom plate and frame(side) assembly for both the 1" and 2" thick billet curing molds.

PROCESSING SPECIFICATION COMPARISONS

NASA SPECIFICATION (KK5) E-AA-H 30.9-1	LOCKHEED CHANGES	REASONS FOR CHANGE
A. MATERIAL AND MIX PROCESSING		
1. Grind Bulk Fiber in hammer mill equipped with 1/32" screen	1. Use .008" screen	1. Less balling problem with shorter fibers
2. Dry Fiber. Then weigh requisite amount of Fiber and PBI resin and blend in "V"-blender for 10 minutes	2. "V" Blend for 20-25 min.	2. Better mix.
3. Hammer-mill above mixture using a 1/16" screen	3. Use 20 mesh screen (.034" opening)	3. Less Balling problem.
4. Add requisite amount of microballoons to mixture and "V" blend 2 hrs. at 24 RPM for a 1 lb. batch	4. None	4. Not applicable
5. Examine 3 randomly slected samples of mixture under 35X magnification. No fiber agglomerates should be present and components should be completely and uniformly dispersed	5. Carried out after step 5	5. Final inspection to insure desirable mix processing.
6. No sieving specified.	6. Sieve through 20 mesh screen	6. Gives better and more homogeneous mix in preform mold.

TABLE V

PROCESSING SPECIFICATION COMPARISONS

NASA SPECIFICATION (KK5) E-AA-H 30.91	LOCKHEED CHANGES	REASONS FOR CHANGE
B. PREFORMING		
1. Pack mixture uniformly in a molding frame, place in an oven at 250°F for 20 min.	1. Molding frame with metal stops pre-heated to 225±10°F, then packed uniformly with mixture and placed in pre-heated oven at 250°F for 25 min.	1. Resin is brought to temperature sooner, hence staging is begun sooner and advances further. Stops guarantee volume.
2. Frame placed in hydraulic press preheated to 250°F. Apply 15 psi pressure for 20 min. Allow preform to cool to 150°F under pressure before removing from the press.	2. Same, except 40 psi pressure applied and held for 25 min.	2. Higher pressure required to obtain 30 lb/ft^3 end density. Longer time used to further advance resin.
C. CURING		
1. Wrap preform in 2 layers of 181 style glass cloth and 2 layers asbestos sheet. Place a 1/8" thick aluminum plate on top and bottom of preform and seal structure in a Teflon bag.	1. Place preform in a stainless steel mold with 2 layers of glass cloth and asbestos on all 6 sides. The open top end of mold is fitted with a silicone rubber sheet and covered and boxed with an open 1/8" Al. Plate.	1. Mold guarantees flat, exact size, repeatable, specimen.
2. Preform cured under vacuum in an oven according to the following schedule: 15 min. at 250°F; 20 min. at 300°F; 30 min. at 350°F, 400° and 500°F respectively; then 20 min. at 600°F.	2. Preform cured under vacuum in an oven according to the following schedule: 15 min. at 250°F; 45 min. at 300°F; 60 min. at 350°F, and 400°F, respectively, 45 min. at 500°F, then 20 min. at 600°F.	2. Curing extended at lower temperatures to stage resin and minimize resin flow to help guarantee high resin content of finished billet.

TABLE V (Cont'd)

PROCESSING SPECIFICATION COMPARISONS

NASA SPECIFICATION (KK5) E-AA-H 30.9-1	LOCKHEED CHANGES	REASONS FOR CHANGE
D. POST CURING		
Cured billet placed in stainless steel container with inert gas purge. Glass cloth placed on both sides of billet inside container. Post cure in oven: RT 600°F 2 hours 600 700°F 1 hour 700°F 20 minutes 700 800°F 1 hour 800°F 20 minutes 800 850°D 30 minutes — 5 hours 10 minutes	Billets cured between graphite panels, separated from the panels by 2-3 thickness of glass cloth. Cured in oven in an inert atmosphere (N_2). Post cure schedule RT 600°F 2 hours 600 700°F 1 hour 40 minutes 700°F 20 minutes 700 800°F 1 hour 40 minutes 800°F 20 minutes 800 950°F 2 hours 30 minutes 950°F 30 minutes	To help guarantee better heating equilibrium throughout 1" billet post curing time extended at lower temperatures. This prevented warpage of billet. The extended heating cycle to 950° allowed for desired crosslinking density. At 850°F this was not realized.

TABLE V (Cont'd.)

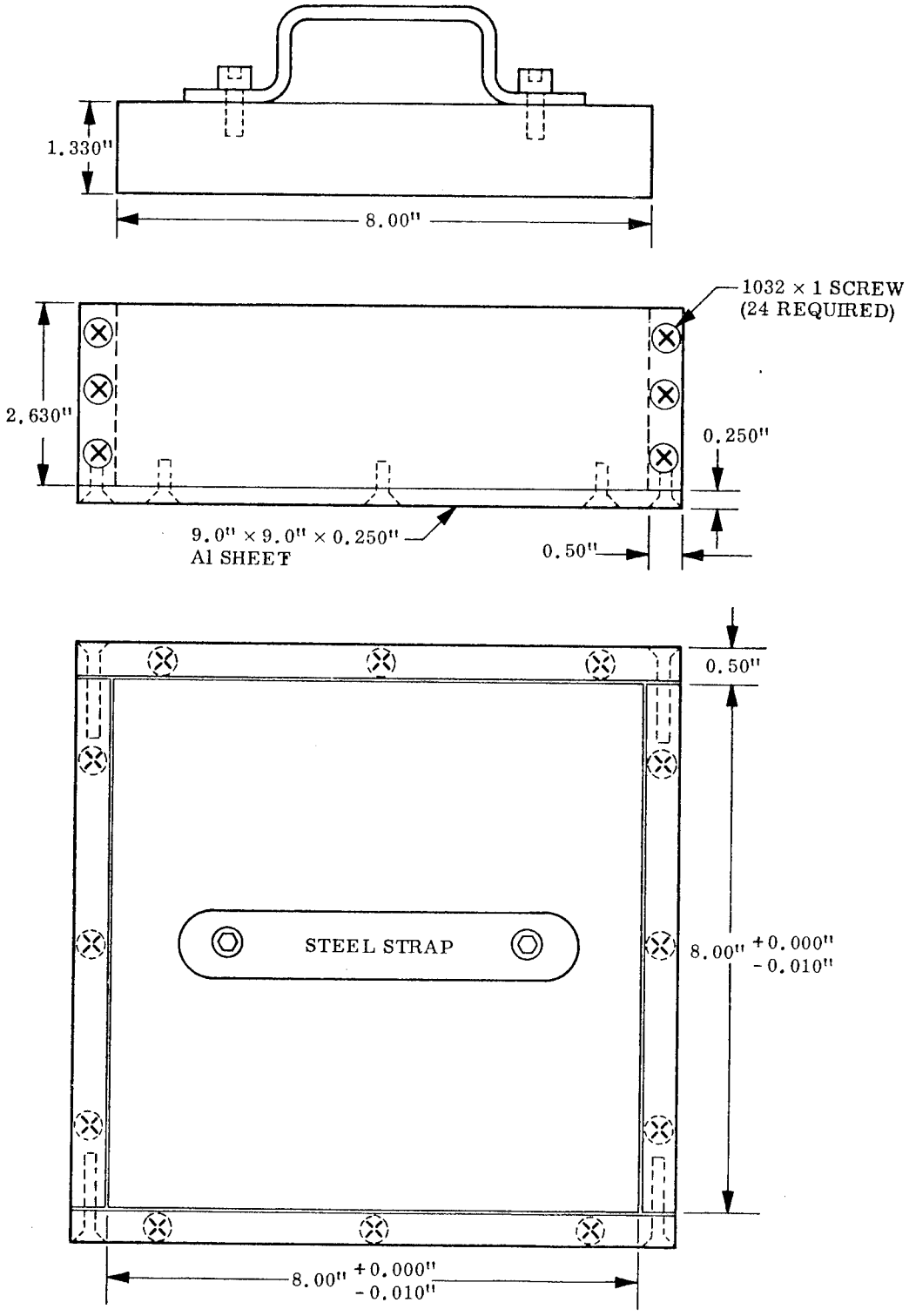


Fig. 5 1-inch PBI-Carbon Composite Billet Preform Mold (Aluminum)

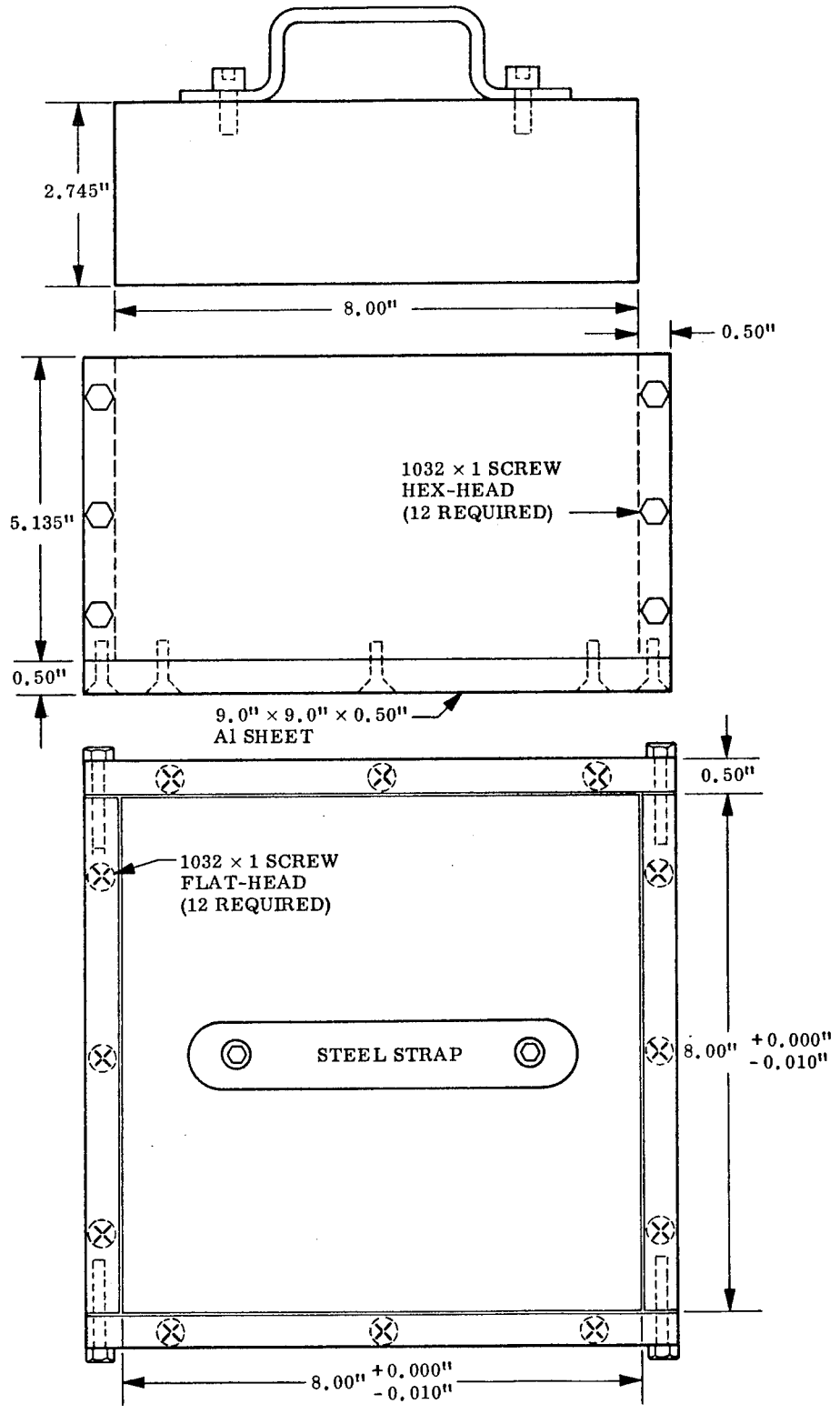


Fig. 6 2-inch PBI-Carbon Composite Billet Preform Mold (Aluminum)

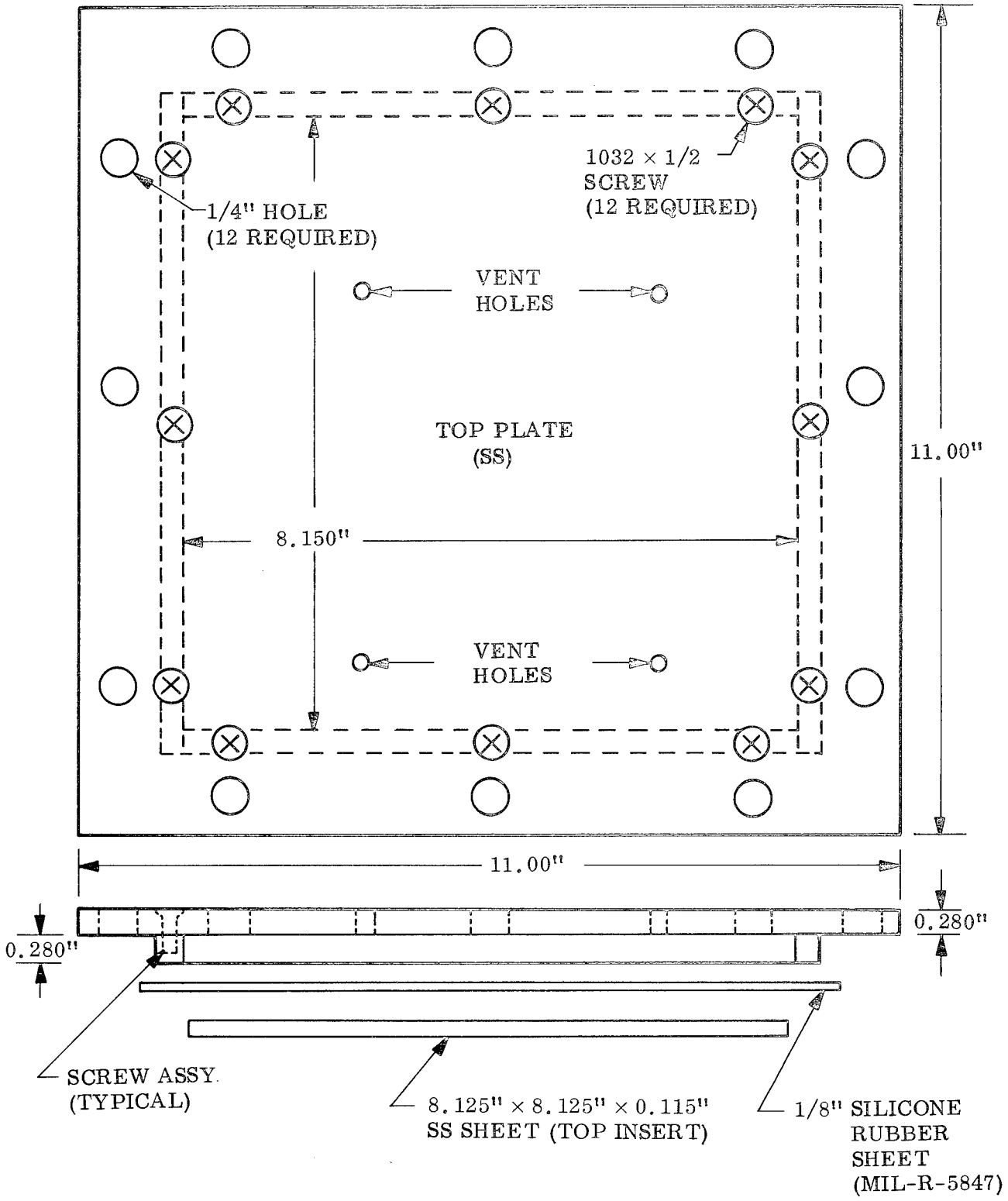


Fig. 7 Top Assembly, PBI-Carbon Composite Cure Mold

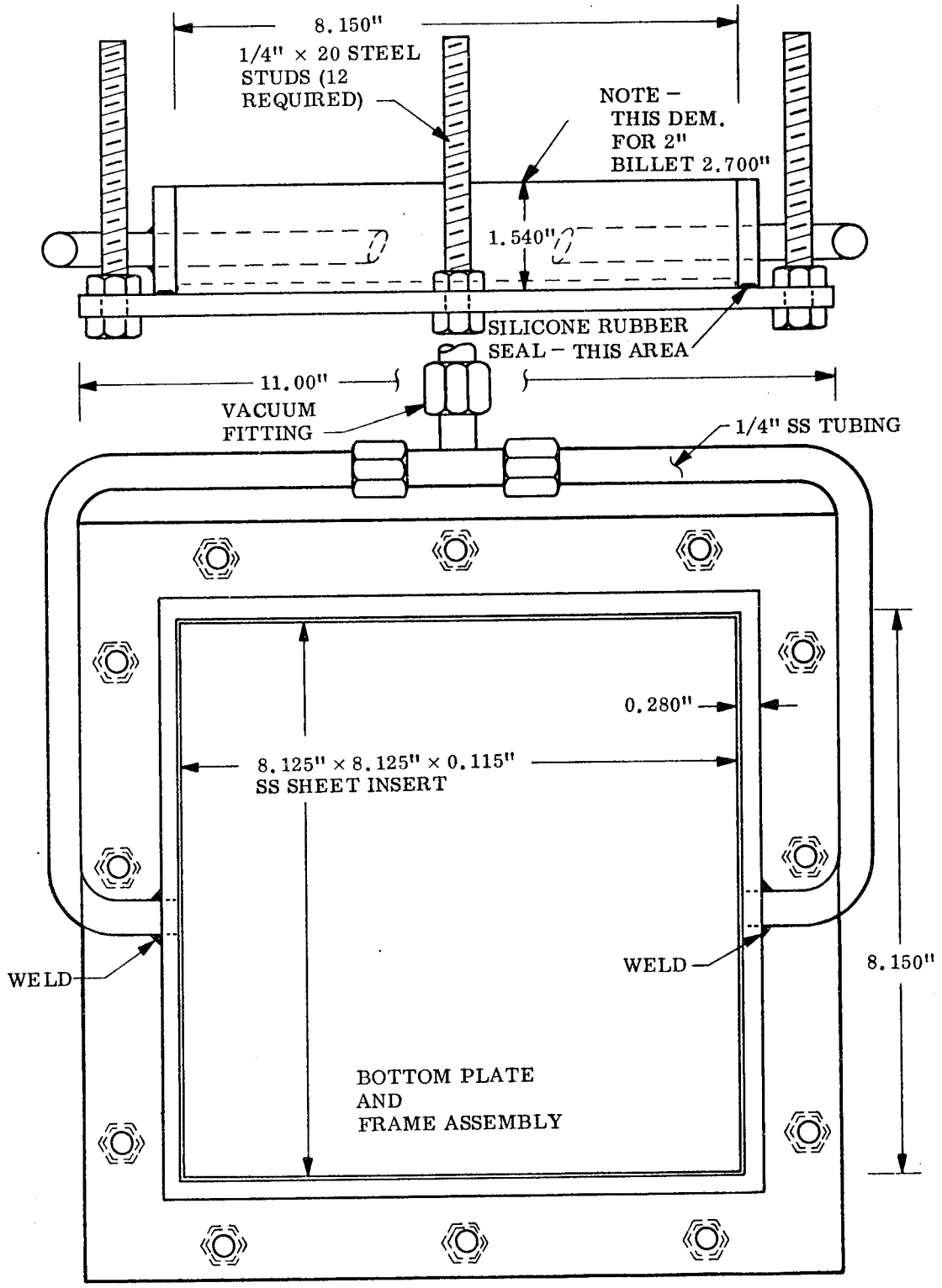


Fig. 8 1-inch PBI-Carbon Composite Billet Cure Mold (Stainless Steel)

The utilization and pictures of the tooling are shown in Figs. 9-11. Fig. 9 shows the preform mold, in which stops are placed on each side and then loaded with a given weight of the homogeneous mix of components used to prepare the billets. The lid or top is inserted into the filled bottom and hydraulically pressed as described in the specification in Appendix "A".

Fig. 10, Picture "A" shows the 1" thick billet tooling spread out on the table before assembly. The preform billet is surrounded on all six sides with asbestos sheet and glass fabric as described in Appendix "A" and placed into partially assembled curing mold as shown in Picture "B", Fig. 10.

The 1/8-inch metal plate is inside the mold over the glass cloth covered preform billet, followed by the silicone rubber diaphragm which extends over the top sides of the mold. The diaphragm is held in place by bolting the top of mold on. Fig. 11, picture "A" shows the assembled mold with unbolted top in place. Note the four vent holes on the top surface which allow diaphragm to compress the billet at 15 psi when vacuum is applied during the curing. Fig. 11. picture "B",shows the assembled curing mold from a side view in which the rubber diaphragm may be seen.

3.2.2 Billets Delivered

The program called for the production and delivery of 27 billets. Of these the dimension call-out for six billets was 2" x 6" x 6" and for twenty-one billets 1" x 6.5" x 6,5". Of the six 2" billets, three billets contained phenolic microballoons and three contained glassy carbon microballoons in their compositions. Of the twenty-one 1" billets, 10 were prepared with

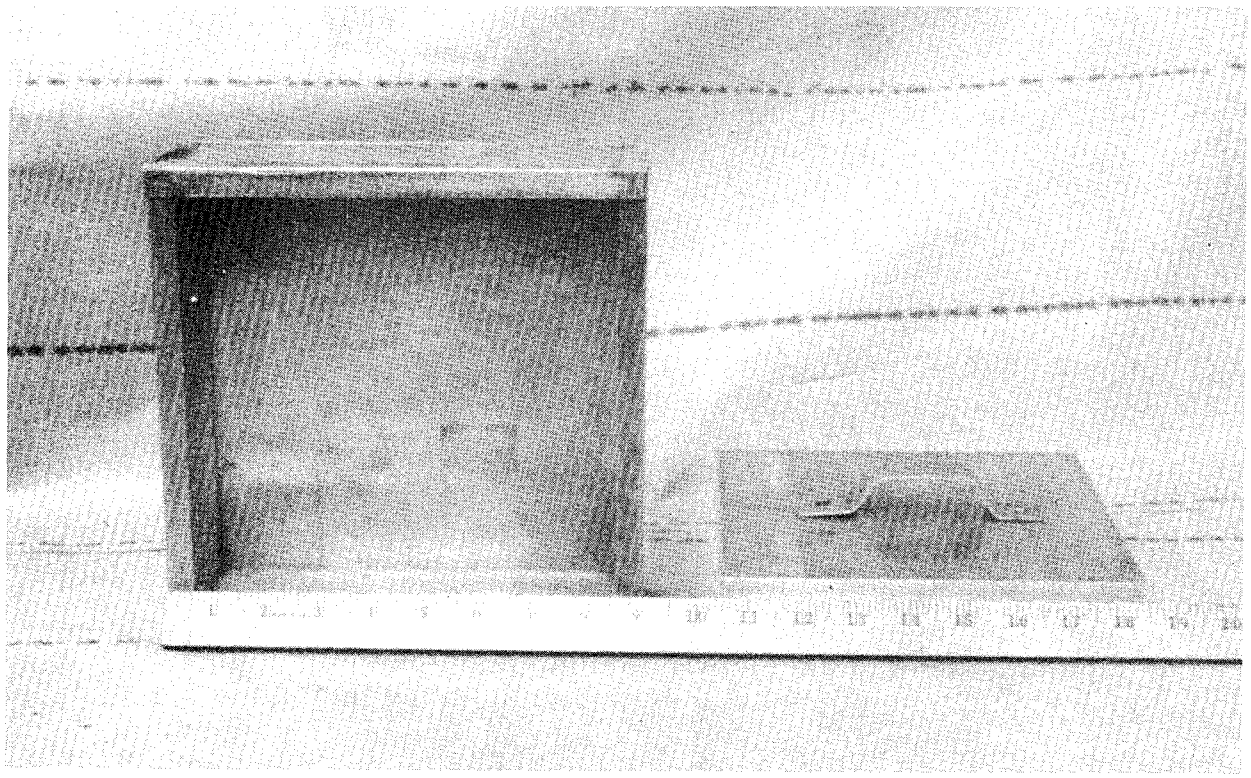
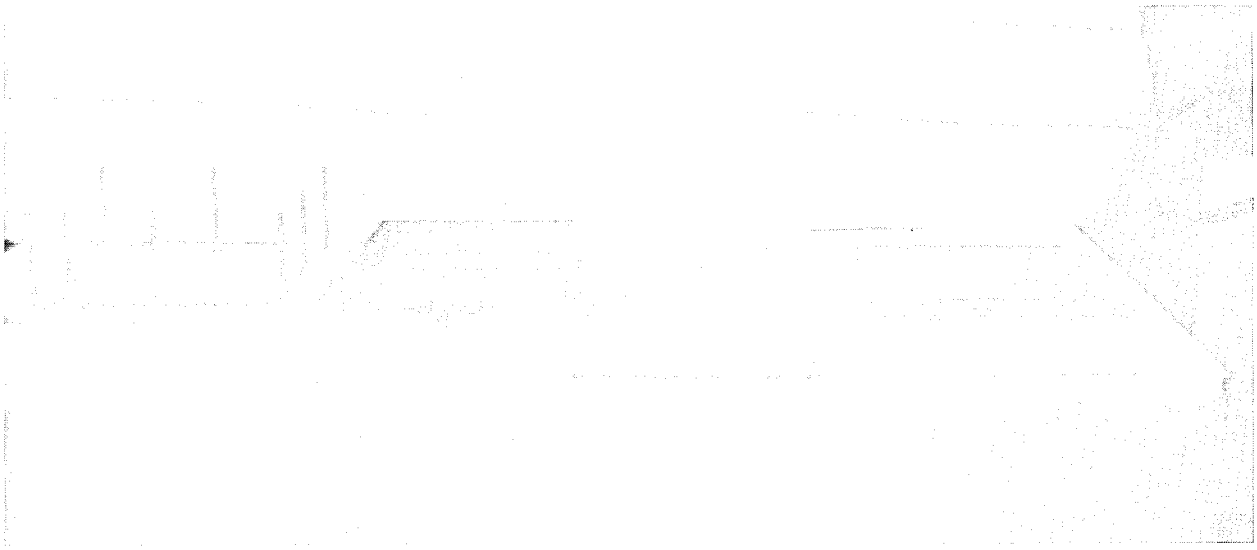
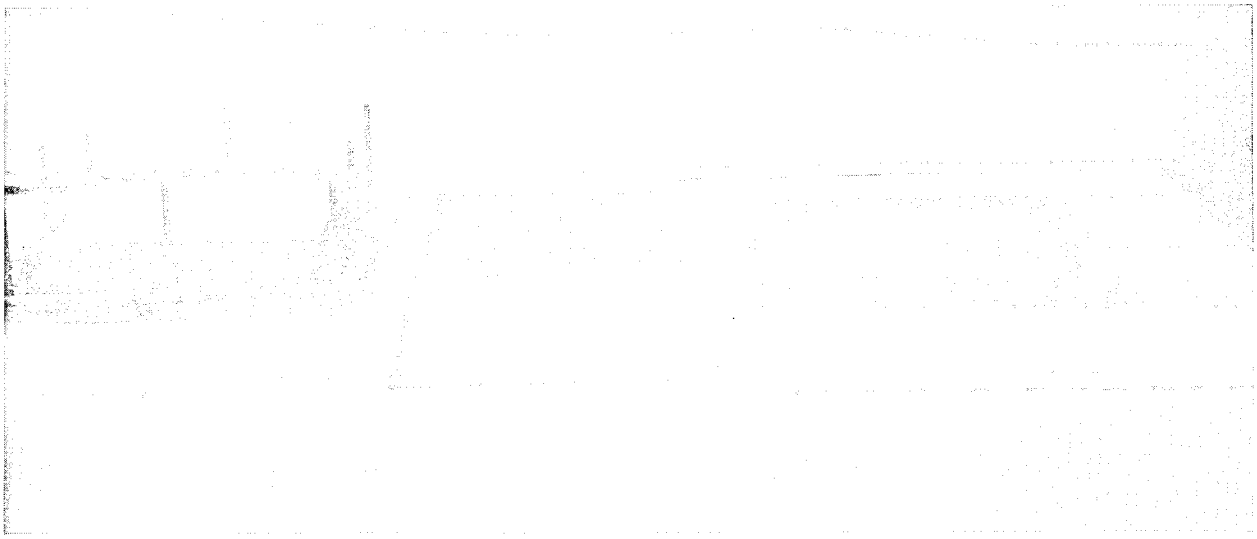


Fig. 9 Preform Mold

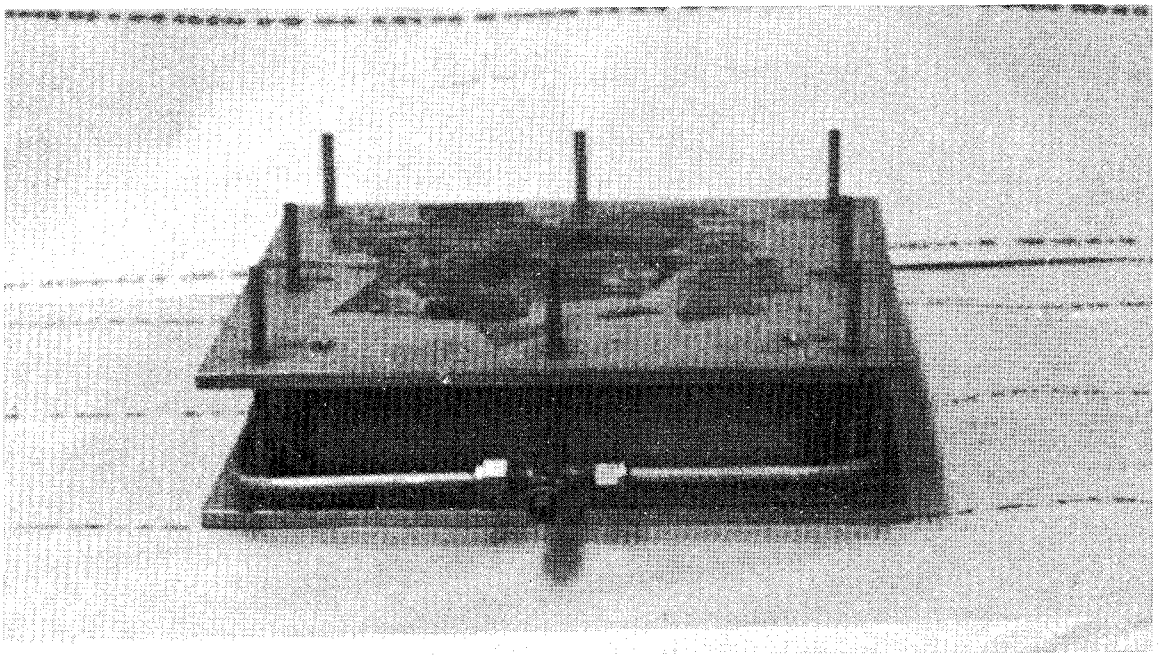


Picture "A" Unassembled Curing Mold

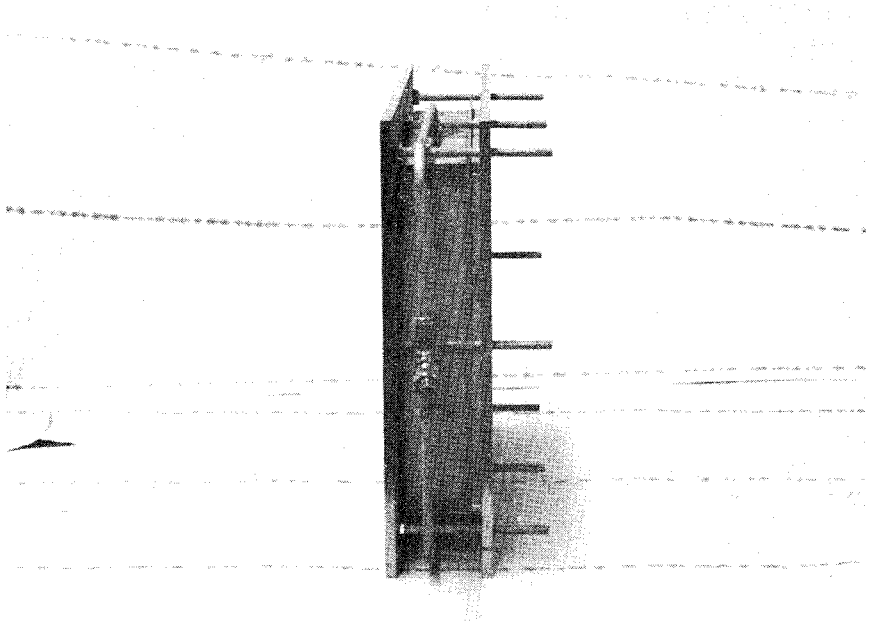


Picture "B" Partially Assembled Curing Mold

Fig. 10 Unassembled and Partially Assembled Curing Mold



Picture "A" – Top View



Picture "B" – Side View

Fig. 11 Top and Side View of Assembled Curing Mold

phenolic microballoons and 11 with glassy carbon microballoons.

In Table VI the twenty-seven billets, which were delivered, are designated and listed. The dimensions of the billets are given in the table as are the weight, volume, density, compressive strength, percent open cell structure, etc. The test results of the billets will be discussed in the next section where the test procedures and methods are outlined.

3.2.3 Billet Test Procedures and Results

The finished post cured billets required inspection and testing before delivery. The procedures involved, methods, and results follow.

3.2.3.1 Visual Inspection

All the 1" thick billets delivered were originally prepared in an 8"x8"x1.1" configuration. These were cut down to approximately 6.5"x6.5"x1.05" thickness for delivery. During the cutting, visual and microscopic inspection of the sectioned and unsectioned parts of the billets were performed. There was no appearance of cracks in any of the specimens or their parts. The billets were in general homogeneous in appearance.

Earlier undelivered billets were inhomogeneous until processing changes in material and mix processing were instituted as shown in Table V. These earlier billets showed sections in which the carbon fibers were aggregated into fiber balls.

BILLETS DELIVERED

Billet Designation	Date Deliv.	Nominal Dimensions inches	Density	Porosity % Open Cell Content	Grain Direct Compressive Strength psi	Micro Balloon Type	PBI Batch	Wt. Gms.
1. LP1-26	9/ 3/69	6.5x6.5x1	30.9	25	-	Phenolic	92	-
2. LP1-27	"	"	30.6	29.5	2337	"	92	-
3. LP1-28	"	"	30.9	27		"	92	-
4. LG1-33	"	"	29.4	31	4380	Glassy carbon	92	-
5. LG1-34	"	"	29.7	37	-	"	92	-
6. LG1-35	"	"	29.6	32	-	_	92	-
7. LP2-42	9/23/69	6.2x6.3x2.0	31.2	30.5	2709	Phenolic	92	-
8. LG1-39	11/ 3/69	6.7x6.7x1	30.7	42	3397	Glassy carbon	93	398
9. LG2-40	"	6.7x6.7x1	29.0	-	3368	"	93	382
10. LG2-41	"	6.7x6.7x1	29.0	44.5	3355	"	93	398
11. LG2-1-50	"	6.2x6.2x2.1	32.0	36	4598	"	93	700
12. LG2-2-56	12/ 5/69	6.2x6.2x2.1	30.4	35.8	3450	"	92	660
13. LG2-2-57	"	6.5x6.3x2.2	29.3	43	3240	"	92	655
14. LP2-2-58	"	6.2x6.3x2.0	30.3	28.5	3040	Phenolic	92	625

TABLE VI

Billet Designation	Date Deliv.	Nominal Dimensions inches	Density lbs/ft^3	Porosity % Open Cell Content	Grain Direct Compressive Strength psi	Micro Balloon Type	PBI Batch	Wt. Gms.
15. LP2-2-59	12/ 5/69	6.3x6.2x2.0	30.0	34.5	2170	Phenolic	92	620
16. LP1-2-60	12/11/69	6.7x6.7x1.1	30.1	27.5	2600	"	92	390.5
17. LP1-2-61	"	6.6x6.7x1.1	31.0	28.8	3010	"	92	387.5
18. LP1-2-62	"	5.7x6.6x1.1	30.7	31.5	3300	"	92	377.5
19. Lp1-2-63	"	6.6x6.7x1.1	30.1	33	2640	"	92	286.5
20. LG1-2-51	12/11/69	7 x6.6x1.1	32.0	43.5	-	Glassy carbon	93	431
21. LP1-3-80	5/27/70	6.7x6.7x1.1	31.5	27	4155	Phenolic	93	398
22. LP1-3-90	"	7.0x6.7x1.1	31.5	39.5*	3670	"	93	406
23. LP1-3191	"	6.7x6.5x1.1	30.4	28	2850	"	93	398
24. LG1-3-92	"	6.7x6.7x1.2	29.9	24*	3510	Glassy carbon	93	416
25. LG1-3-93	"	6.7x6.7x1.2	30.2	24*	3645	"	93	416
26. LG1-3-94	8/21/70	6.7x6.8x1.1	30.4	37	4042	"	93	414
27. LG1-3-95	"	6.7x6.7x1.1	30.8	33.8	3855	"	93	423

* O_c vs R graphed with two points instead of usual three.

TABLE VI (Cont'd)

3.2.3.2 Compressive Strength

Compressive strength measurements followed ASTM D-1621-64.

Compression tests were performed on specimens taken from each billet. Specimens were 1.00 x 1.00 x 1.00 inches nominally.

Tests were performed on an Instron Tester Model TTCL. A CF Load Cell was attached to the machine base.

Specimens were measured with caliper prior to loading. The loading rate was approximately 0.2-inches/min. in all tests. Loading was stopped and the pan lifted after achieving a peak load followed by a decrease in load. Peak stress was calculated for each specimen.

A typical compression test run on representative samples of billets containing phenolic microballoons (LP1-27) and glassy carbon microballoons (LG1-33) gave the following results:

Grain Direction	Perpendicular to Grain Direction	Grain Direction
LP1-27	LP1-27	LG1-33
2348	1870	4990
2328	1910	3500
2413	1890	4230
2260	___	4800
Avg. 2337	Avg.1890	Avg.4380

In the case of LP1-27 the load was applied in the grain direction or direction in which the molding stress was applied in preparation of the billets.

When compression test was run perpendicular to the grain direction the compressive strength was approximately 19% lower. Two typical curves of the different foams tested are shown in Fig. 12.

In the above cases the glassy carbon microballoons in billet LG1-33 at a slightly lower density imparted a much greater compressive strength compared to the phenolic microballoon containing billet LP1-27. In all the billets shown in Table VI, the compressive strength measurements were on samples in the grain direction, since this was the direction of expected stress on utilization.

The phenolic microballoon containing billets showed compressive strengths ranging from 2170 psi to 4155 psi with a billets' average of 2952 psi. In comparison the glassy carbon microballoon containing billets' compressive strength ranged from 3240 to 4958 psi with an average of 3713 psi. The trend indicates that the glassy carbon microballoons containing billets are the stronger of the two.

3.2.3.3 Density

Each billet specimen is accurately cut and sanded to obtain a flat and straight edged surface. Loose particles are removed with compressed air. The two long axes of a given billet are then measured with a precision caliper in a minimum of four places to the nearest .001" while the short axis is measured in a minimum of eight places to the nearest .001". The values of the respective axes are obtained by averaging the measured values. The volume is the multiple of the three different axes and is

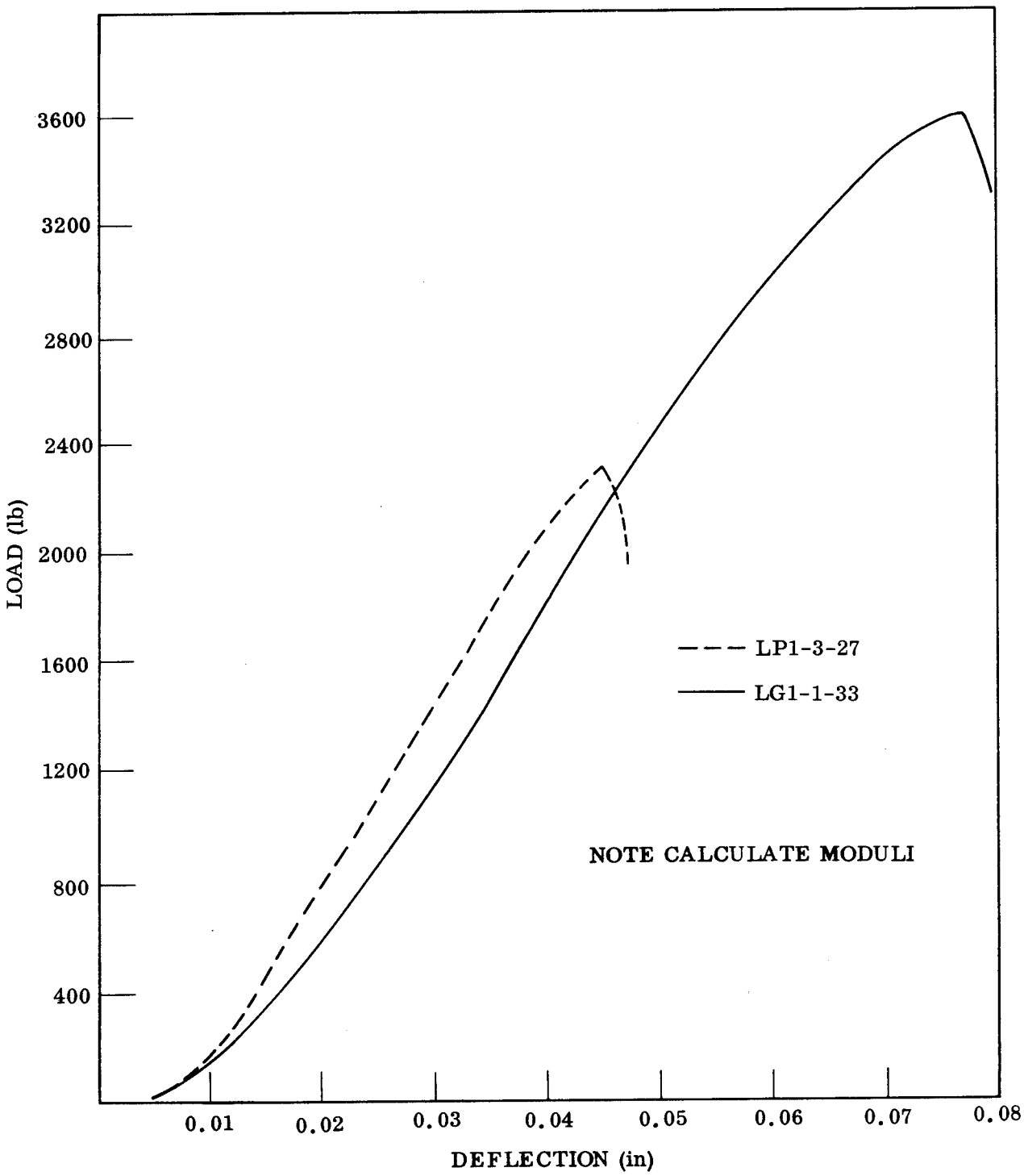


Fig. 12 Representative Graphs of Compression Test Results

divided into the weight (in grams) of the billets. The quotient multiplied by 3.8 gives the billet bulk or apparent density in lbs/ft^3.

$$\text{Density} = \frac{\text{Billet Weight (gms)}}{\text{Volume (in}^3\text{)}} .3.8 = \quad lbs/ft^3$$

The specified bulk density was 30 ± 2 lbs/ft^3. The density range obtained for the 27 delivered billets was 29.0-32 lb/ft^3. Of these 81.5% were in the 30 ± 1 lb/ft^3 range. Most of the billets soon after preparation were cut, weighed and the volume measured. The density was then computed. Some of the last studies on the cylinders demonstrated the foam's ability to both pick up moisture from the air on standing with some concomitant increase in volume. The net result, however, was greater proportionate weight increase with consequent increase in density. The billets could be returned to initial density state by heating at 350°F for 1-2 hours to remove absorbed water. This will be discussed in section 3.3.3.3.

3.2.3.4 Thermogravimetric Analysis (TGA)

TGA measurements of billets containing glassy carbon microballoons and phenolic microballoons respectively, were carried out. The TGAs are shown in Figs. 13 and 14 respectively. It is interesting to note that both billets pick up water, as shown by the weight loss which starts below 100°C and asymptotes off at 200°C.

In the case of the glassy carbon microballoon containing billet, the water content loss represents 4.8%. At 1000°C, the billet loses 17.1% weight or 17.1 - 4.8 = 12.3% net loss. This net weight loss begins to occur at 590°C. By 800°C the curve has begun to shallow and weight loss

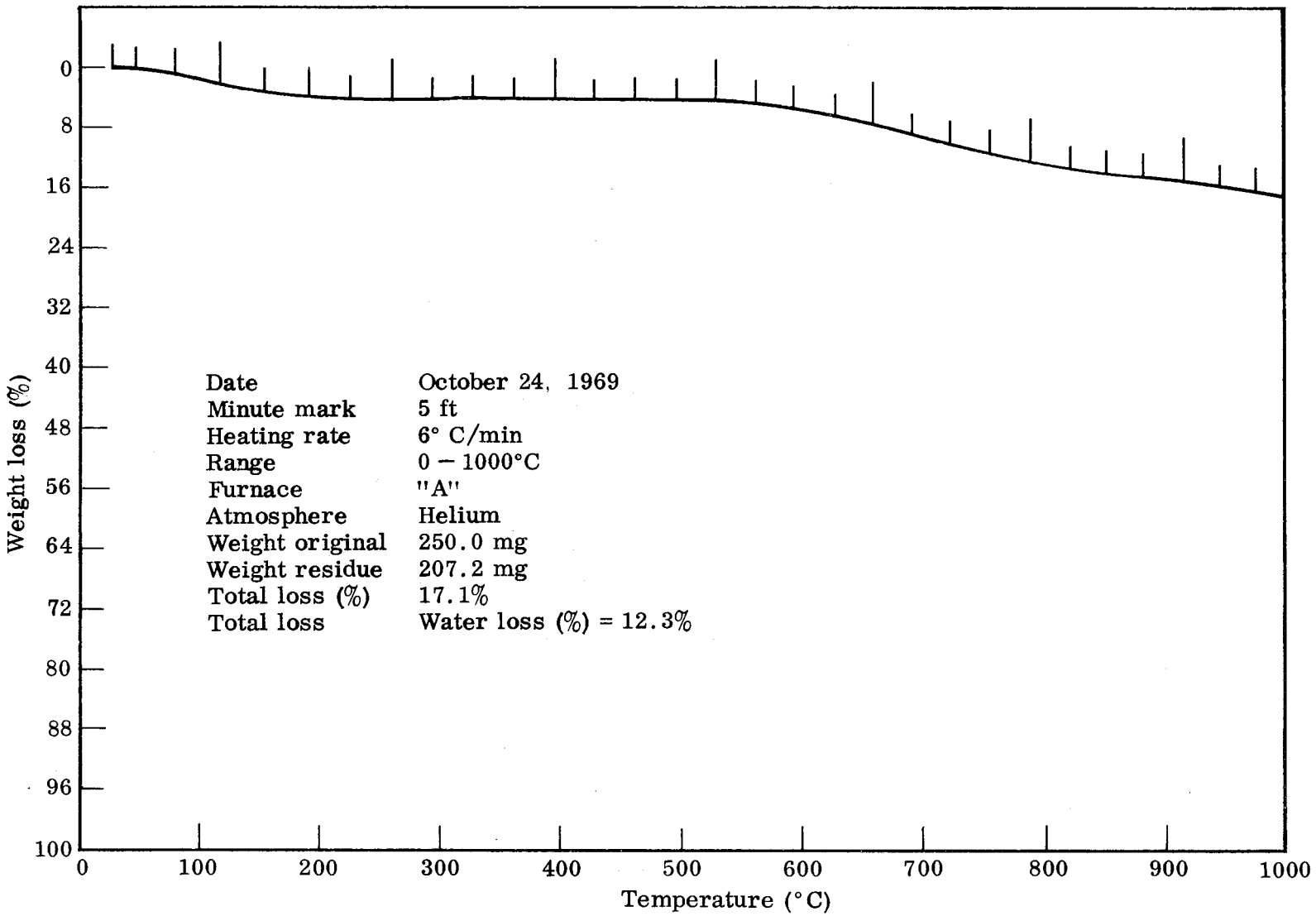


Fig. 13 Thermogravimetric Analysis of PBI, Carbon Fiber, Glassy Carbon Microballoons, Billet

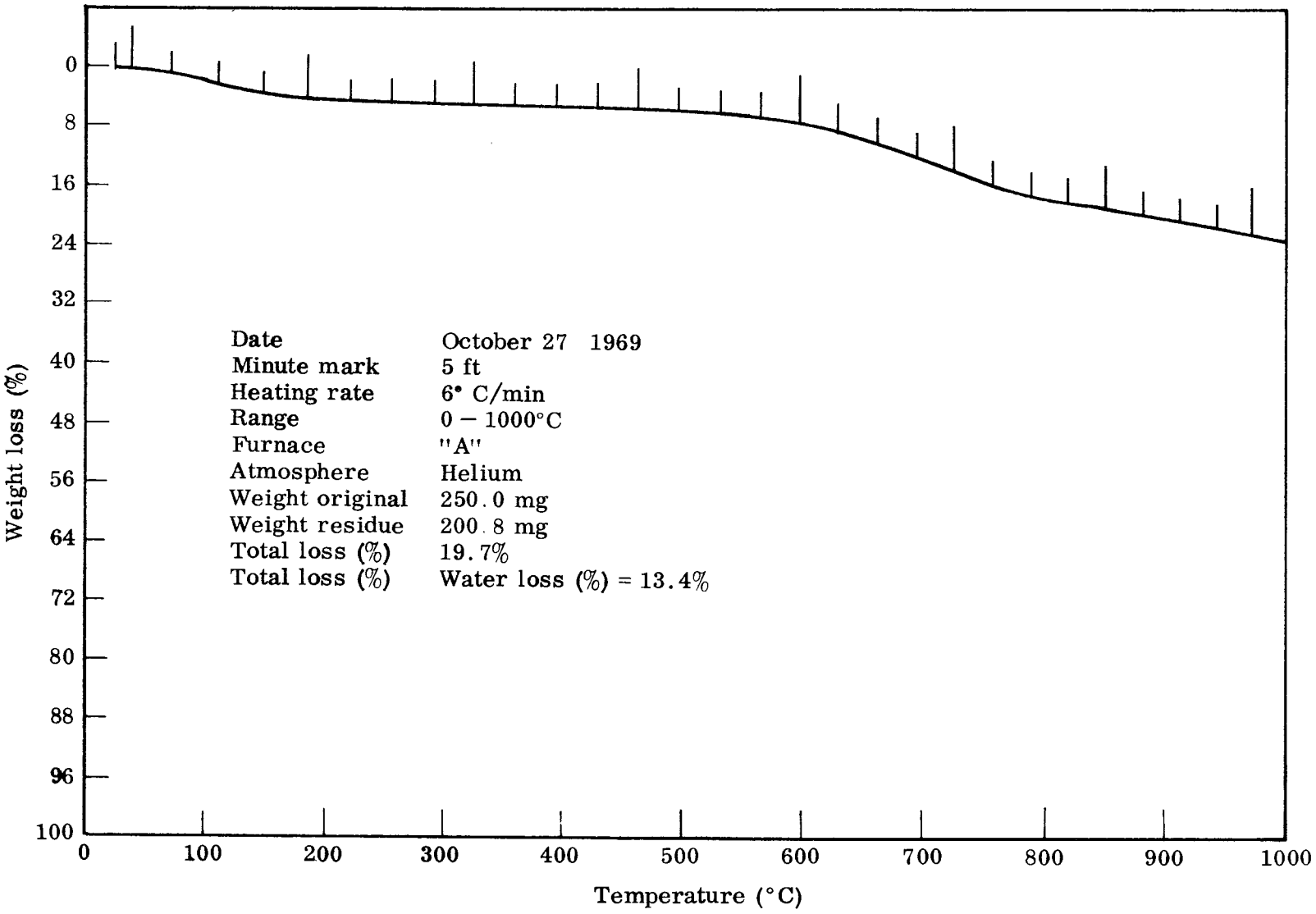


Fig. 14 Thermogravimetric Analysis of PBI, Carbon Fiber, Phenolic Microballoons, Billet

rate has diminished, so that between 800°C and 1000°C only 4% loss is noted.

In the case of phenolic microballoon containing billet the water content loss may be 1.6% higher or 6.4%. At 1000°C the billet loses 19.7% weight or 19.7 - 6.4 = 13.3% net loss. The net loss also perceptably begins at 590°C. By 800°C the curve has begun to shallow out so that between 800-1000°C the billet loses 5.6% by weight. The reason for this greater weight loss with the phenolic microballoon containing billet is due to the greater weight loss of these microballoons compared to the glassy carbon microballoons. This is further aggravated by the oxygen decomposition molecules which are given off by the phenolic degradation.

3.2.3.5 Elemental Analysis of Billets Containing PBI

Duplicate elemental analysis runs on post cured billets of the two different compositions containing PBI Batch 92 were carried out. The initial compositions by weight were as follows:

Composition I	Composition II
PBI - Imidite 2801 Batch 92 - 69%	PBI - Imidite 2801 Batch 92, 69%
Hitco "CCA-1" Carbon Fibers - 13%	Hitco "CCA-1" Carbon Fibers - 1/2" 13%
BJO-0930 Phenolic Microballoons 18%	IMSC-Glassy Carbon Microballoons 18%

The analysis obtained of the post cured billet prepared from the above

composition was as follows:

Composition I	Composition II
C - 82.85%	C - 84.85%
H - 3.8%	H - 2.95%
N - 10.6%	N - 11.25%
O - by difference 2.75%	O - by difference .95%

The samples before analysis were dried at 150°F/2 hours in vacuum. This should have removed most of the water. Previous thermogravimetric analyses have shown the rapid absorption of 2.5% water which could be removed at 200°C. It would appear that both compositions may still contain either water, or other elemental impurities of a content which is less than 1%.

The utilization of glassy carbon microballoons instead of phenolic microballoons results in 2% more carbon, .8% less hydrogen, at least 1.8% less oxygen. The results show that at the 950°F or 510°C post cure temperature most, if not all of the nitrogen in the polybenzimidazole still remains, as well as most of the phenolic oxygen in the phenolic resin of the microballoons.

3.2.3.6 Emissivity

Emissivity of representative planar billet samples was measured by using an Infrared Reflectometer Model DB 100, manufactured by Geir Dunkle Instruments, Santa Monica, California.

Billet Types	ϵ
1) Phenolic Microballoon Containing	.91
2) Glassy Carbon Microballoon "	.89
3) " " " " Filled with Polyethylene	.90

3.2.3.7 Porosity, Open Cell Content

Porosity measurements were carried out using a gas technique. The method employed ASTM-1940-62T (Method A2) following the procedures of Harding (4). This entails determining the true volume utilizing a Beckman Air Comparison Pycnometer. The sample is halved, quartered, and the true volume determined at each step. The volume fraction of open cell content O_c is determined by:

$$O_c = \frac{V_o}{V_A} \quad \frac{V_A - V_T}{V_A}$$

V_o = open cell volume

V_A = apparent volume (micrometer)

V_T = true volume (Beckman Air Comparison Pycnometer)

The apparent surface to volume ratios $R = \frac{tS}{V_A}$ for the samples are computed and graphed against the open cell structure values. The true open cell content of the foam, corrected for open cells created by cutting, is determined by extrapolating the "best fit" straight line connecting O_c vs R points to $R = \frac{S}{V_A} = 0$ (the O_c axis intercept)

Examples of such plots using this technique are shown in Fig. 15 for a phenolic microballoon delivered billet and Fig. 16 for a glassy carbon microballoon delivered billet. The calculation and measurements used to obtain these plots are tabulated in Table VII.

Table VI shows the porosity or open cell content obtained for the delivered billets. The porosity of the phenolic microballoon containing billets range from 25% open cell content to 34.5% with one erroneous value at 39.5%. In comparison the porosity of the glassy carbon microballoon containing billets range from 31-44.5% open cell content with two erroneous values at 24%. All three erroneous values stem from too small a sample size when the measurement was made. As a result only two points were available on the O_c vs R graph instead of the three as shown in Figs. 15 and 16.

The explanation for the general lower porosity of the phenolic microballoons versus glassy carbon microballoons containing billet becomes readily explicable when one notes the billet photomicrographs in the next section.

POROSITY MEASUREMENTS AND CALCULATIONS

Code	See Test Specimen	Wt/Cms	DIMENSIONS (in inches) Width	Length	Thick.	Density lb/cu ft	# 1 V_T/cc	# 2 V_T/cc	Gms/cc	S/cm^2	V_A/cc	R	O_c
IP1-2-6	whole	7.8625	1.009	1.009	0.915	32.15	9.91	10.06	0.787	36.964	15.268	2.42	34.63
	1/2	4.7520	1.009	1.008	0.555	32.07	5.91	5.93	0.803	27.569	9.252	2.98	36.01
	1/4	2.4410	0.521	1.008	0.555	31.90	2.98	2.96	0.822	17.726	4.777	3.71	37.83
IG1-3-95	whole	7.8313	0.932	1.010	1.018	31.13	10.32	10.38	0.757	37.642	15.706	2.40	34.10
	1/2	3.7846	0.932	0.488	1.016	31.20	4.96	4.95	0.764	24.484	7.573	3.23	34.57
	1/4	2.1740	0.930	0.488	0.580	31.46	2.82	2.84	0.768	16.460	4.314	3.82	34.40

TABLE VII

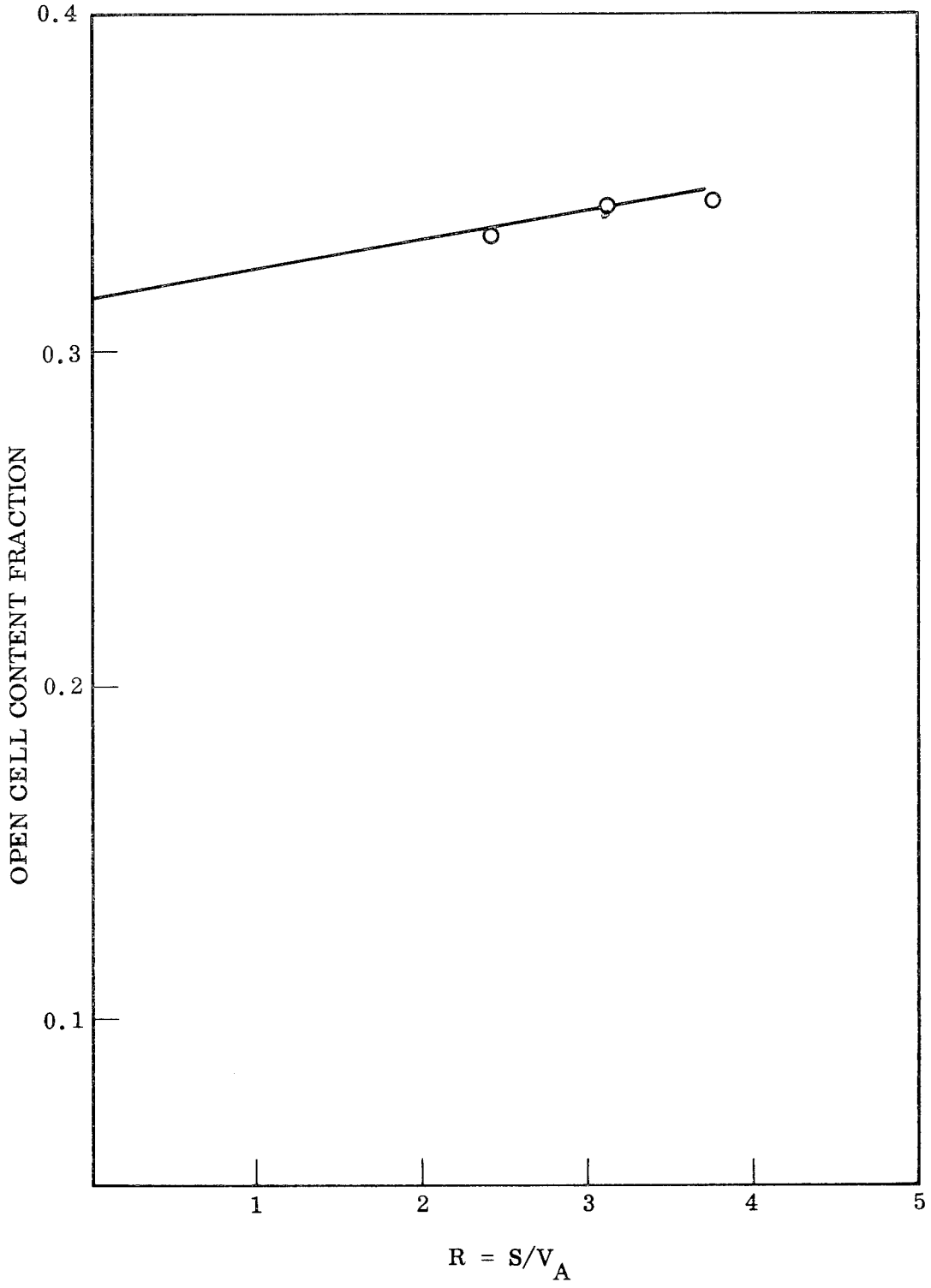


Fig. 15 Porosity of LP1-2-62 Billet

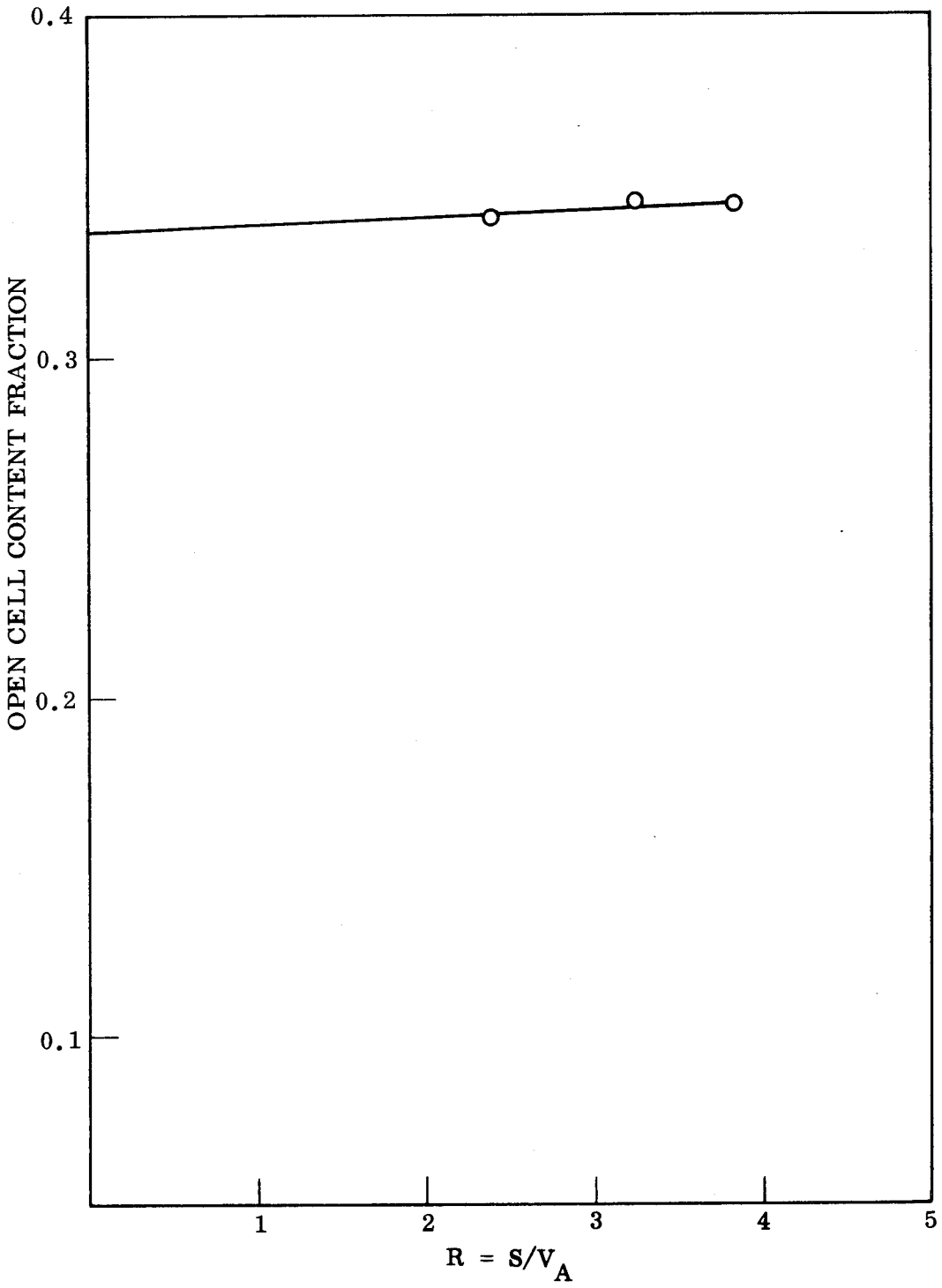


Fig. 16 Porosity of LG1-3-95 Billet

3.2.3.8 Billet Photomicrographs

Photomicrographs, in the form of two views at 100X magnification, of each billet were prepared. Under these conditions little difference could be discerned between the various phenolic microballoons containing billets. In a similar fashion the various glassy carbon microballoons containing billets showed little variation. Major differences, however, between phenolic and glassy carbon containing billets were noted. The billets containing phenolic microballoons show a larger microballoon which often is not spherical in shape while the glassy carbon microballoon is smaller and not misshapen. Based on these pictures it is readily apparent that during the billet curing and post curing stages, the phenolic resin balloons are plastic and flow under the pressure of the gas trapped in the balloon. The glassy carbon microballoon is formed and previously cured to temperature in excess of 1000°C so that the billet curing temperature does not affect it.

This in consequence helps explain why the compressive strength of billets prepared with glassy carbon microballoons are greater than those prepared with phenolic microballoons.

These photomicrographs also help explain the open cell content difference between the billets prepared with glassy carbon microballoons versus those with phenolic microballoons. The explanation for the differences in open cell content between two types of billets is in fact that the phenolic microballoons swell during billet cure, filling in part the interstitial void area. It would seem that most of these phenolic microballoons do not break, hence the low open cell content. The glassy carbon microballoons do

not swell and the interstitial void area remains fairly constant.

Three examples each of both the phenolic microballoon and glassy carbon microballoon containing billets are shown in Figs. 17-22. Figs.17-19 show the latter and figs. 20-22 the former. All the billets showed homogeneous distribution of the resin, microballoons, carbon fibers, and voids.

Fig. 17 Photomicrographs, LG1-34 Billet, 100× Magnification

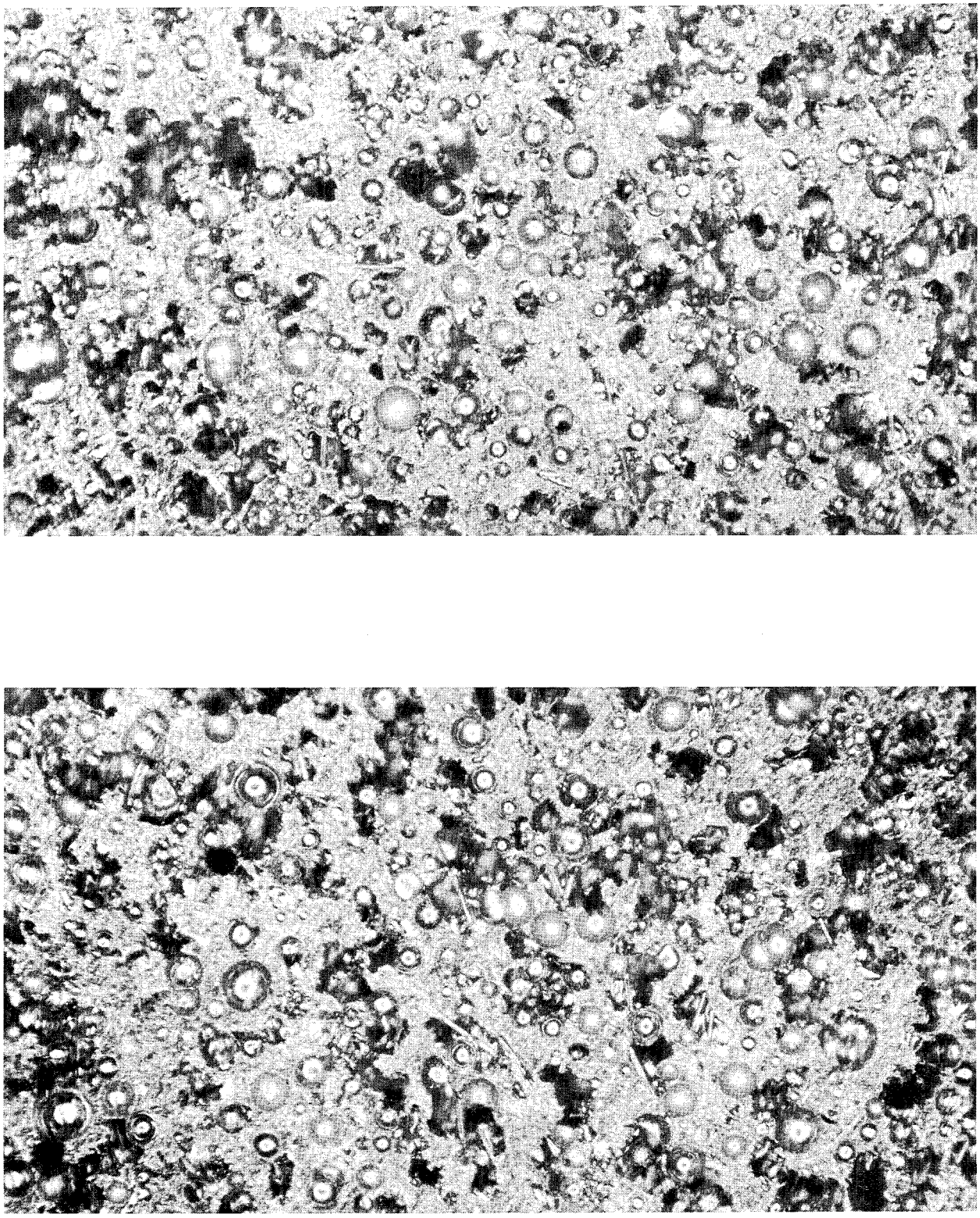


Fig. 18 Photomicrographs, LG-1-33 Billet, 100× Magnification

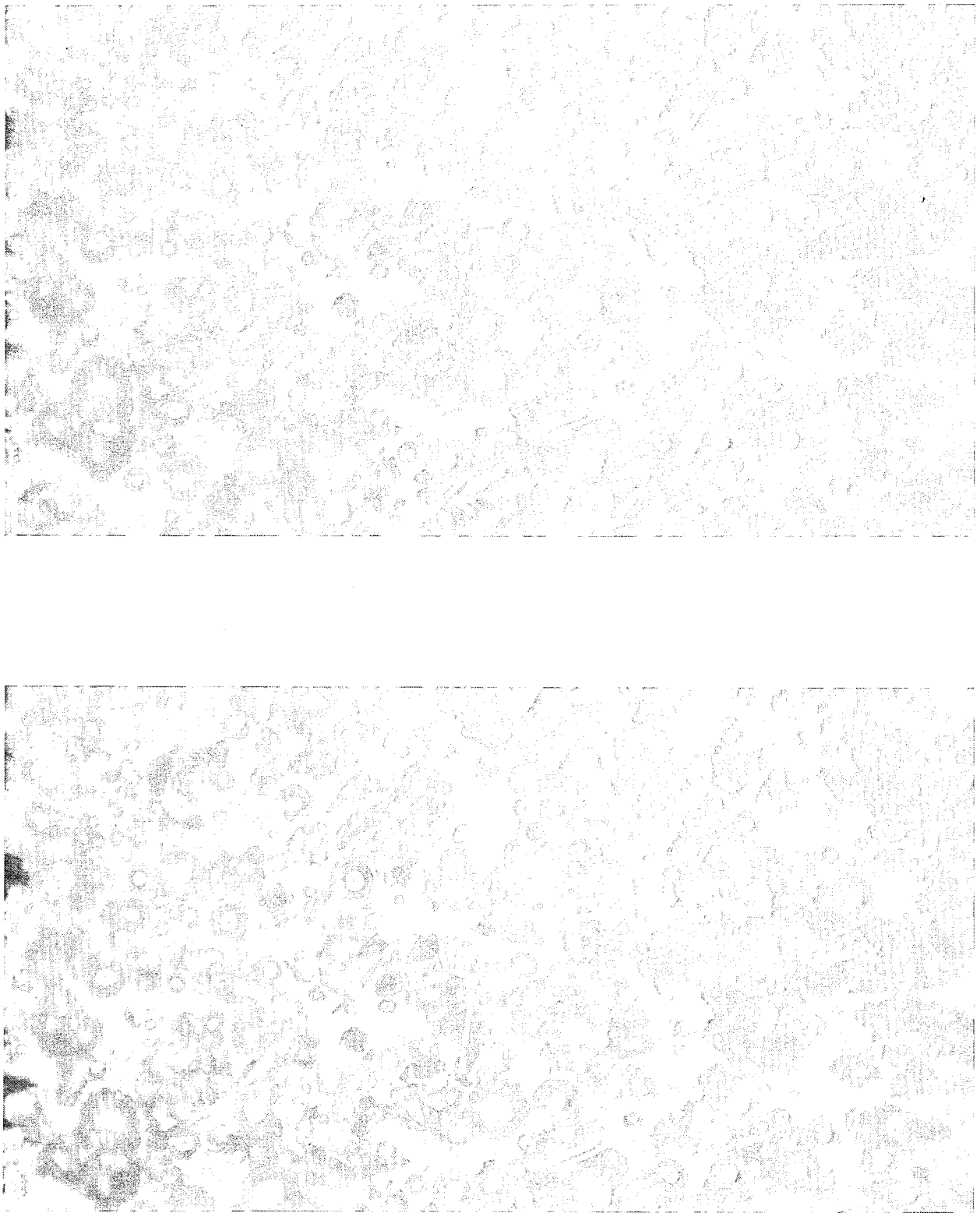


Fig. 19 Photomicrographs, LG-2-2-57 Billets, 100× Magnification

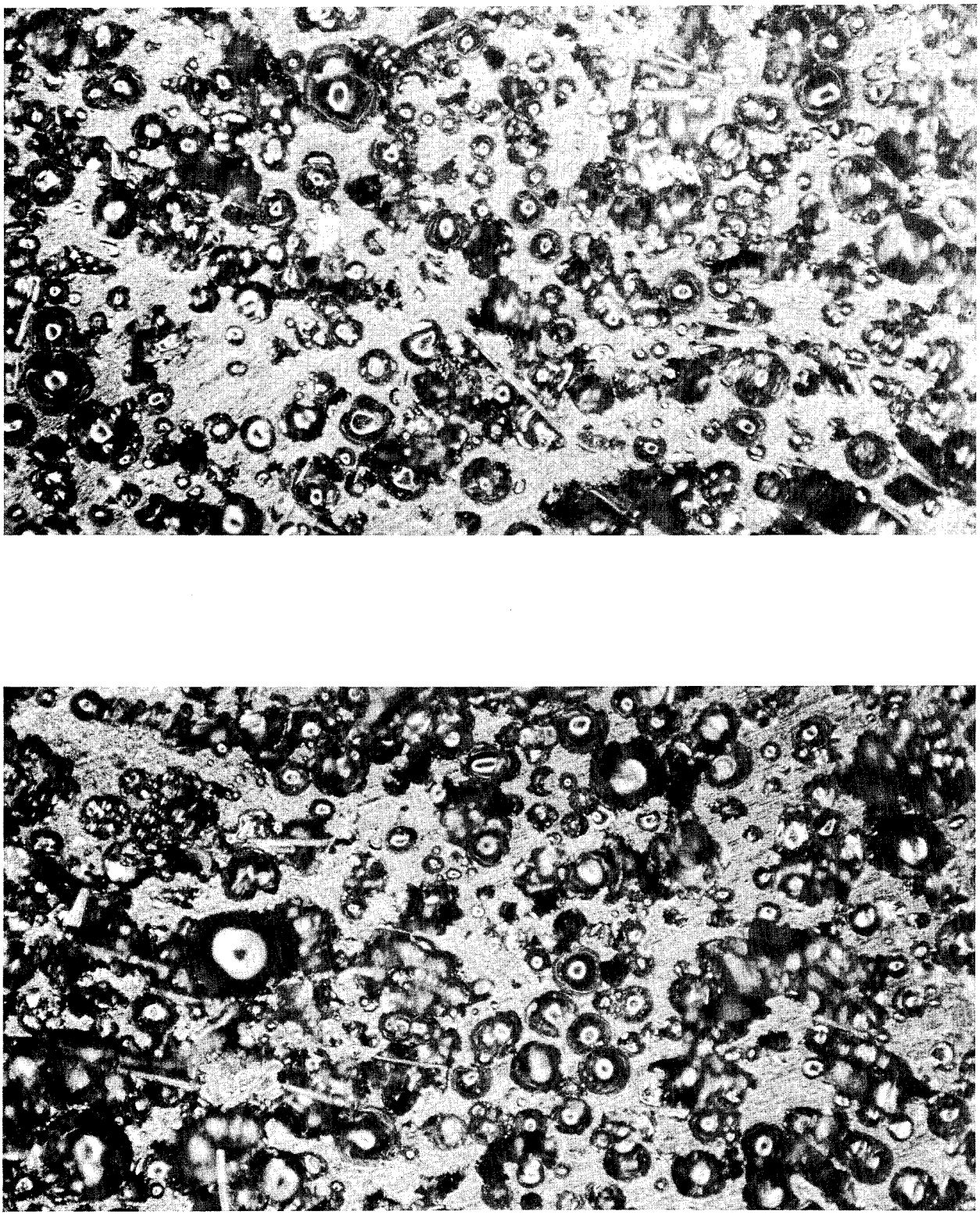


Fig. 20 Photomicrographs, LP1-26 Billet, 100× Magnification

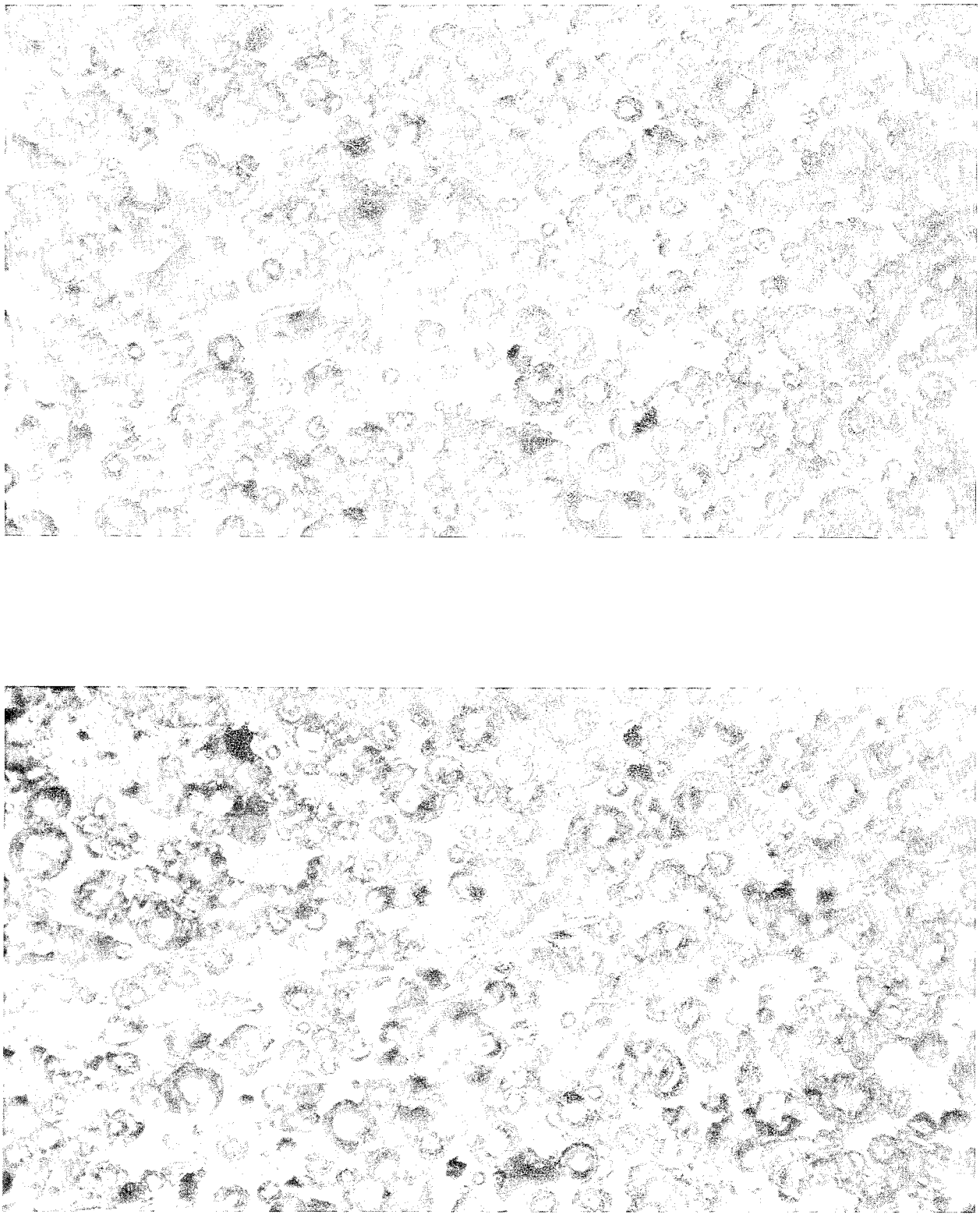


Fig. 21 Photomicrographs, LP1-27 Billet, 100× Magnification

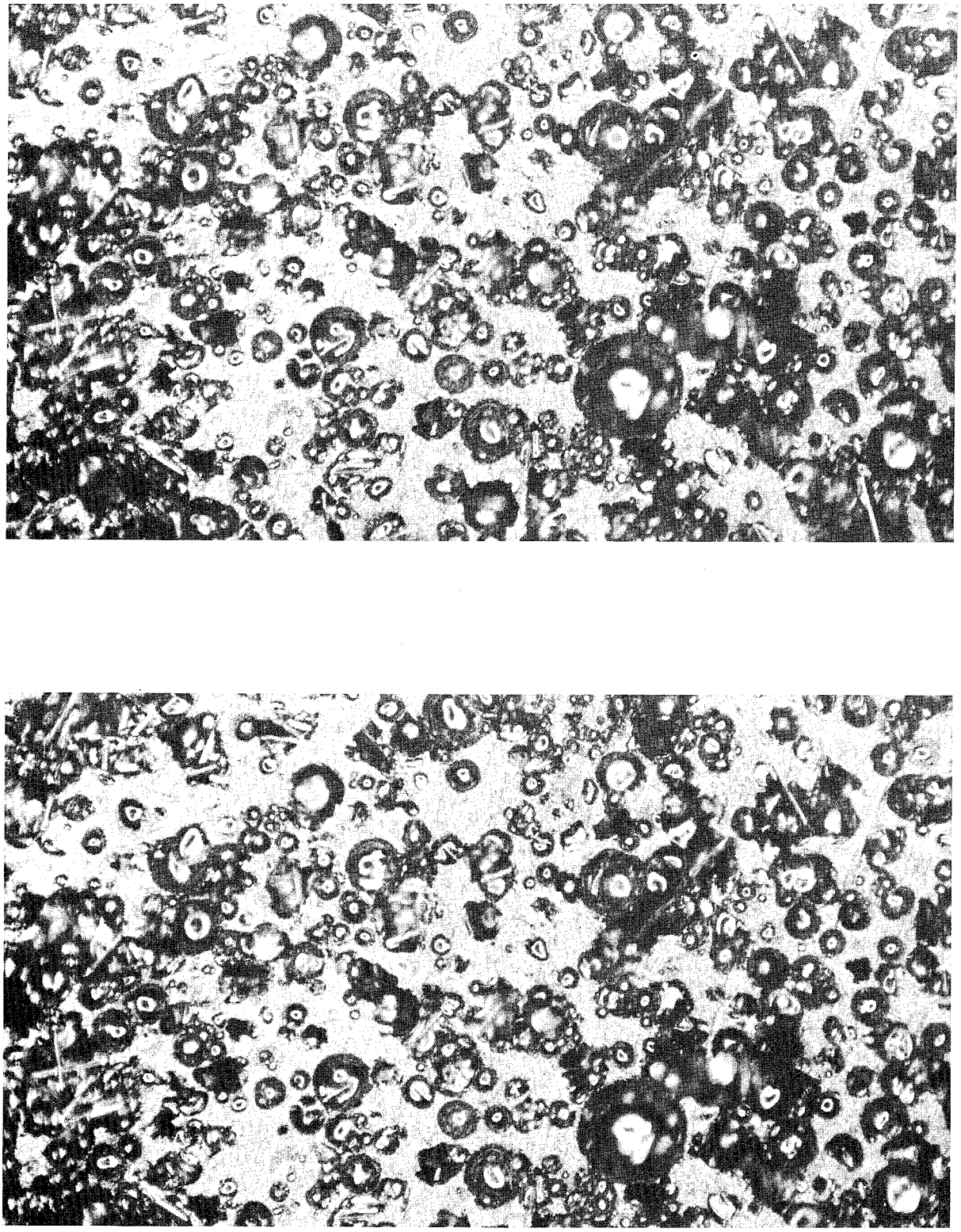


Fig. 22 Photomicrographs, LP-2-2-58 Billet, 100× Magnification

3.3 CYLINDERS

To best test the ablative characteristics of the billets described in section 3.2, required a composite of the same composition in the form of a hollow cylinder. The cylinder model as shown in Fig. 23 (Ames Research Print 2755) was $12"^{+.100"}_{-.000"}$ in length with an O.D. of $3"^{+.250"}_{-.000"}$ and an I.D. of $2"^{+.000"}_{-.100"}$.

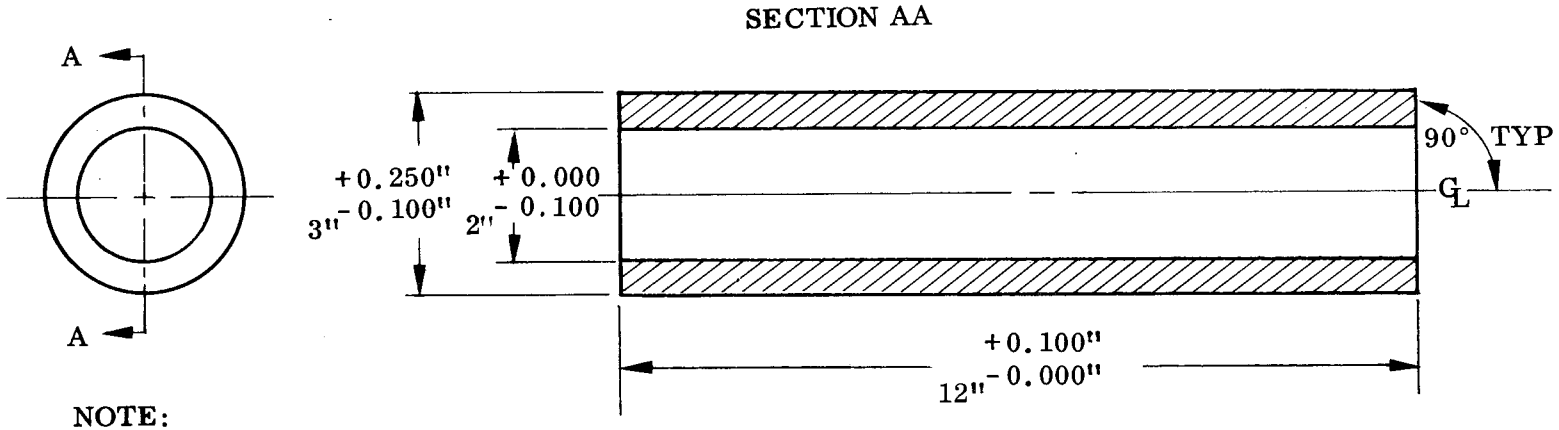
3.3.1 Fabrication and Processing

The fabrication and processing procedure developed by Lockheed to obtain homogeneous, reproducible cylinders of a given density is documented in the cylinder specification in Appendix "B".

Since the cylinders required the same materials and percentage composition used to prepare the billets, there was no difference in materials or in the material and mix processing, as shown in Table V, part "A", section 3.2.1. Indeed all the requirements of tests set forth for the component materials as found in section 3.1.1 hold here as well.

The fabrication and processing to be discussed revolved about tooling to make the cylinders, obtaining cylinders with the same physical properties as obtained for the billets, and successfully machining the billets as required in the Ames Research Center specification print shown in Fig. 23.

This seemingly straight forward goal and its conquest was unfortunately not straight forward. The pitfalls and numerous difficulties encountered will not be covered herein, instead only the successful tooling, processing, and



NOTE:

1. MATERIAL SHALL MEET THE REQUIREMENTS OF SECTION 3.0, SPEC. A-15375, NAS2-5521
2. 5 EACH REQUIRED WITH COMPOSITION SPECIFIED IN SECTION 3.2.1.1
3. 5 EACH REQUIRED WITH COMPOSITION SPECIFIED IN SECTION 3.2.1.2
4. INSIDE DIAMETER CONSTANT STRAIGHT WITHIN 0.010 IN 1200"

Design Engineer, Kourtides

Fig. 23 PBI Ablation Cylinder Model NASA-AR-2755

machining will be discussed.

The drawings for the tooling are shown in Fig. 1 and 2 of Appendix "B". Fig. 1 shows the preform mold while Fig. 2 shows the curing mandrel and mounting schematic.

The utilization and pictures of the tooling are shown in Figs. 24-28A. Fig. 24A shows the unassembled preform tooling. The outer and inner cylinders are both shown as well as one of the inner cylinder heaters and the wire of the other. The last item is the top plunger. In Fig. 24B the composite mix is shown as it is added to the mold and lightly tamped down.

Fig. 25B shows the loaded thermocoupled mold resting in an open clam shell furnace. Fig. 25B shows the furnace and mold positioned in a hydraulic press. The description of the heating and pressurization cycle can be found in the specifications (Appendix "B").

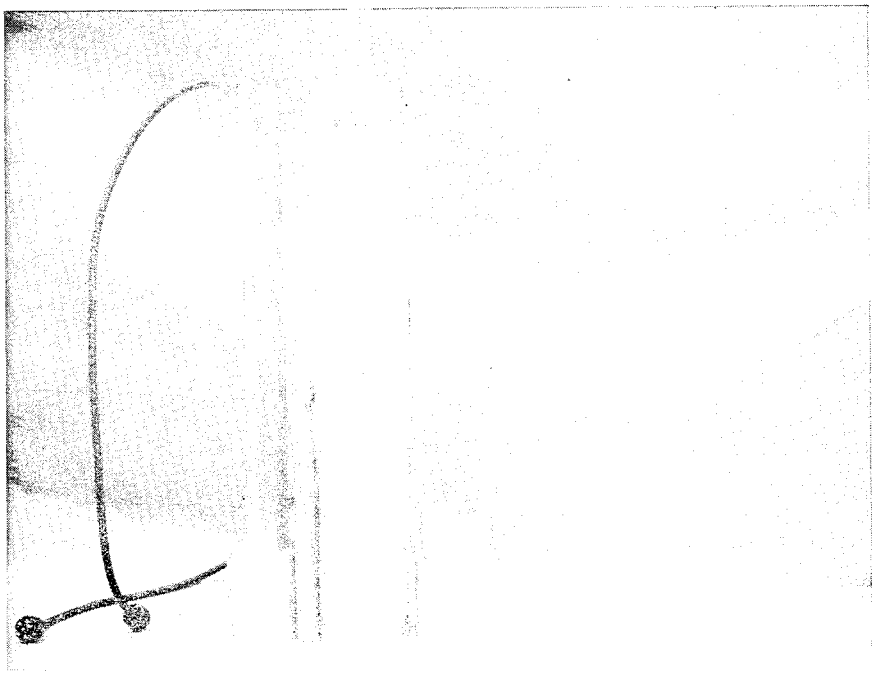
After the preform cylinder has been removed from the mold, curing is carried out. The equipment, tooling, and preform cylinder are shown in Fig. 26A. The vacuum mandrel with its fittings and vacuum holes is shown. Glass cloth used for the mandrel sleeve, and cylinder sleeve, as well as the cylinders are also shown. The silicone rubber bag used to cover the cylinder and the two hose clamps used to fasten it down can also be seen.

Fig. 26B shows the preform cylinder being placed on the glass cloth sleeved mandrel. Fig. 27A shows the mandreled preform cylinder with the metal ends in place being wrapped in an outer glass cloth sleeve. In Fig. 27B one sees the rubber bag being drawn over and fitted on the mandreled preform cylinder.

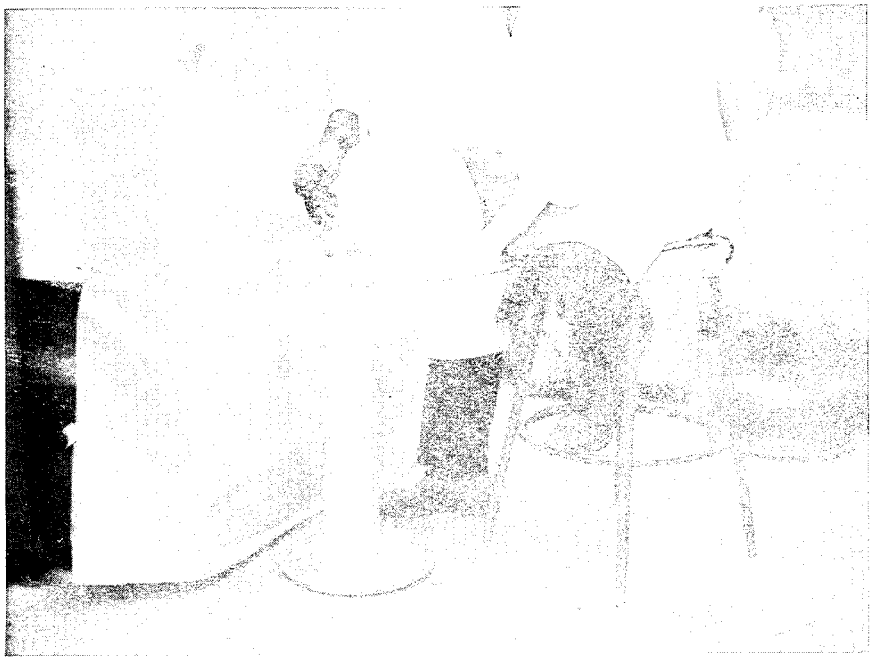
In Fig. 28A we see the clamped rubber bag in place and the preform ready for vacuum attachment and curing.

After curing and postcuring as specified in Appendix "B" the cylinder must be machined to the sizes specified in Fig. 23 and to accomplish this special tooling was built; the drawing for this is shown in Fig. 3, Appendix "B".

In Fig. 28B one sees the internal bore of the cylinder being machined to the required internal diameter. In Fig. 29A and B we see the machining of the outer diameter of the cylinder from two different positions.

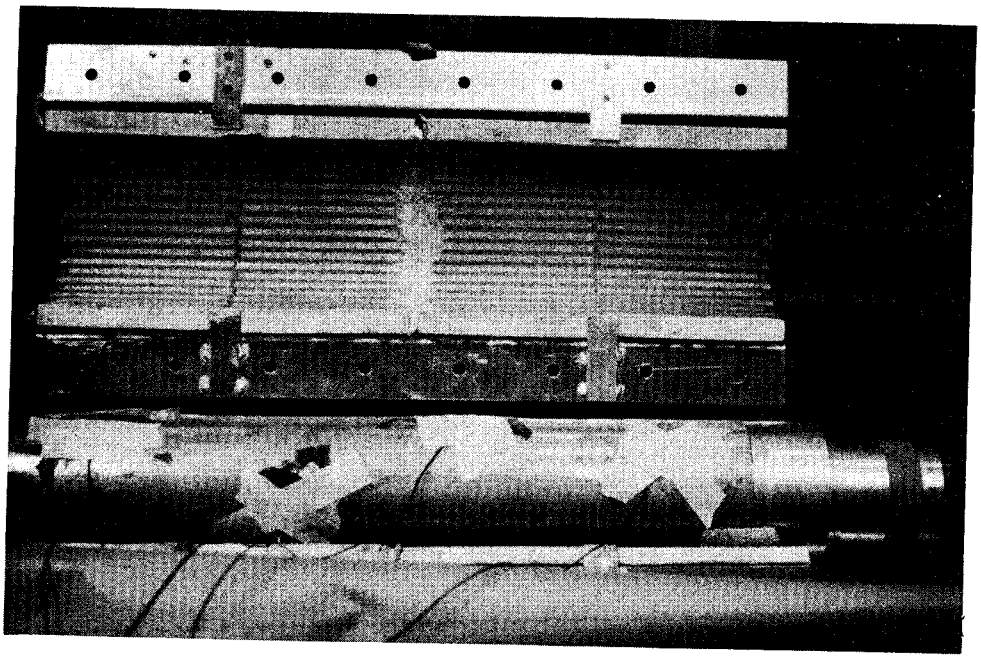


a. Unassembled Mold

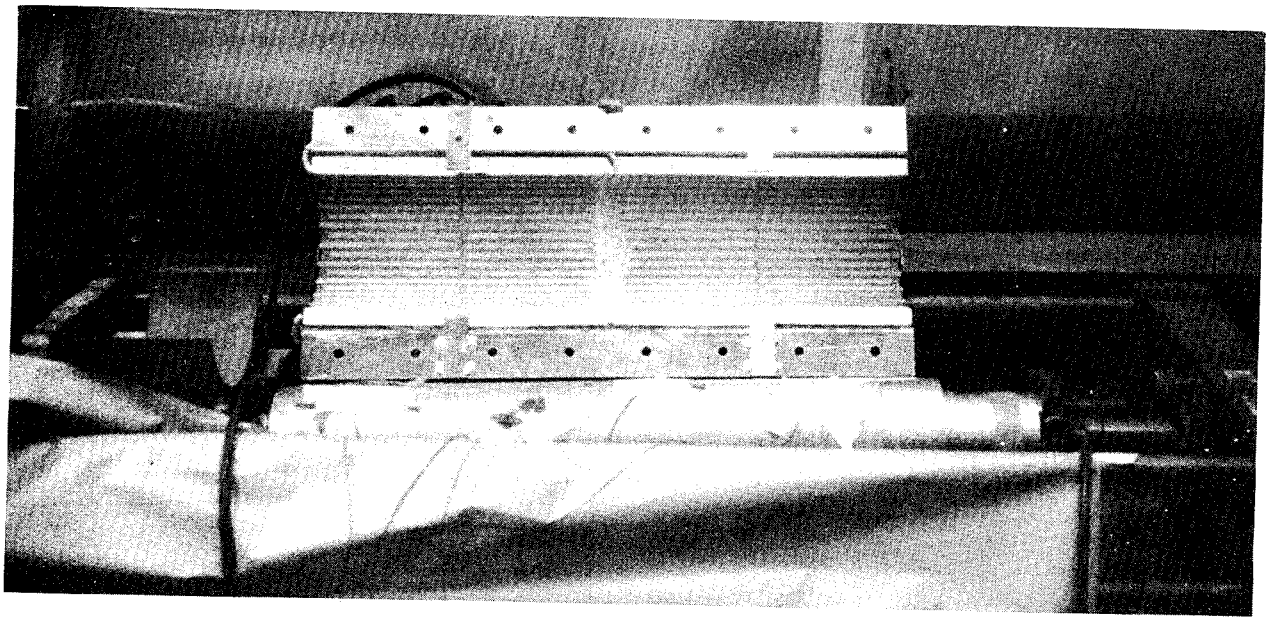


b. Filling Mold

Fig. 24 Preform Cylinder Mold

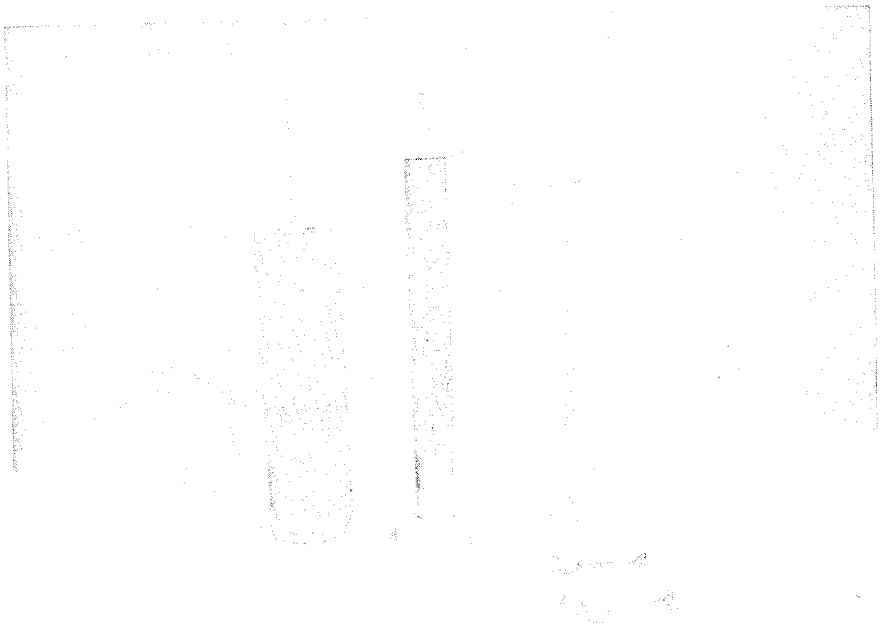


a. Preform Mold in Clam Shell Furnace

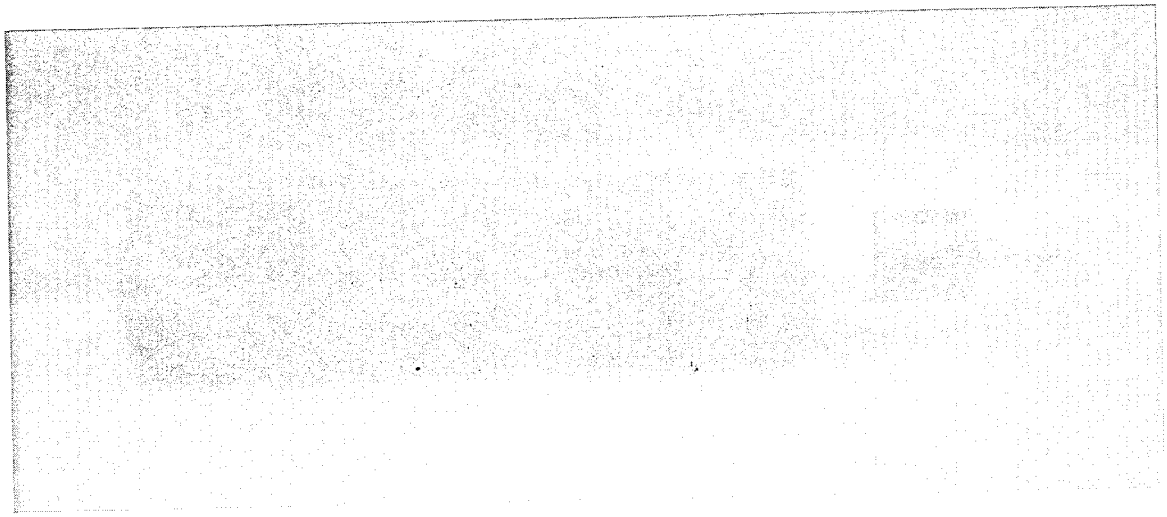


b. Mold and Furnace in Hydraulic Press

Fig. 25 Preform Mold in Hydraulic Press Furnace

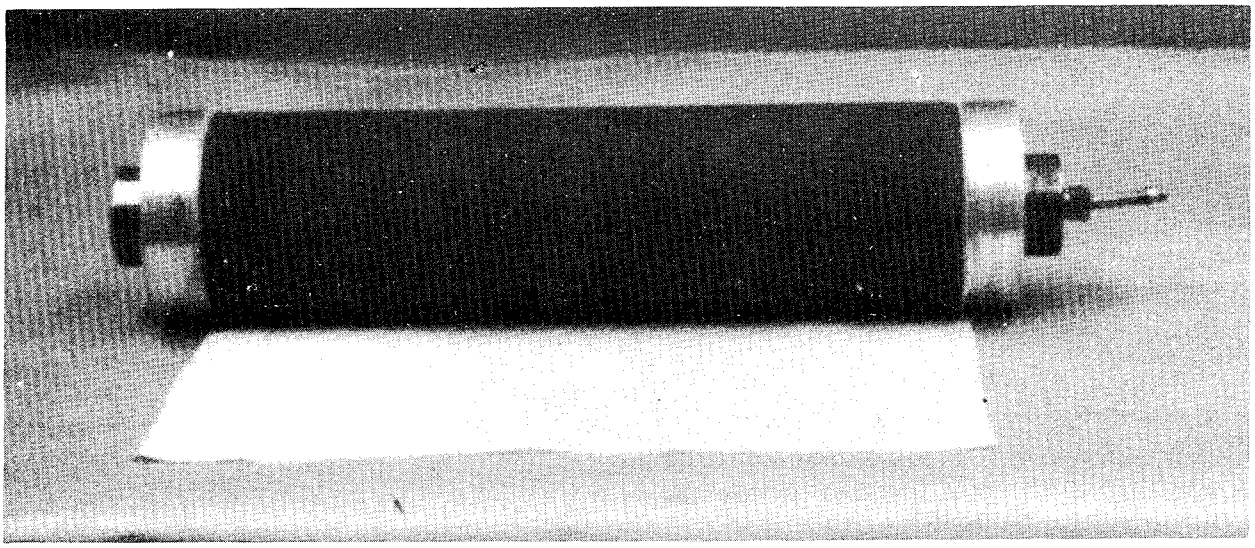


a. Cylinder and Unassembled Curing Tooling

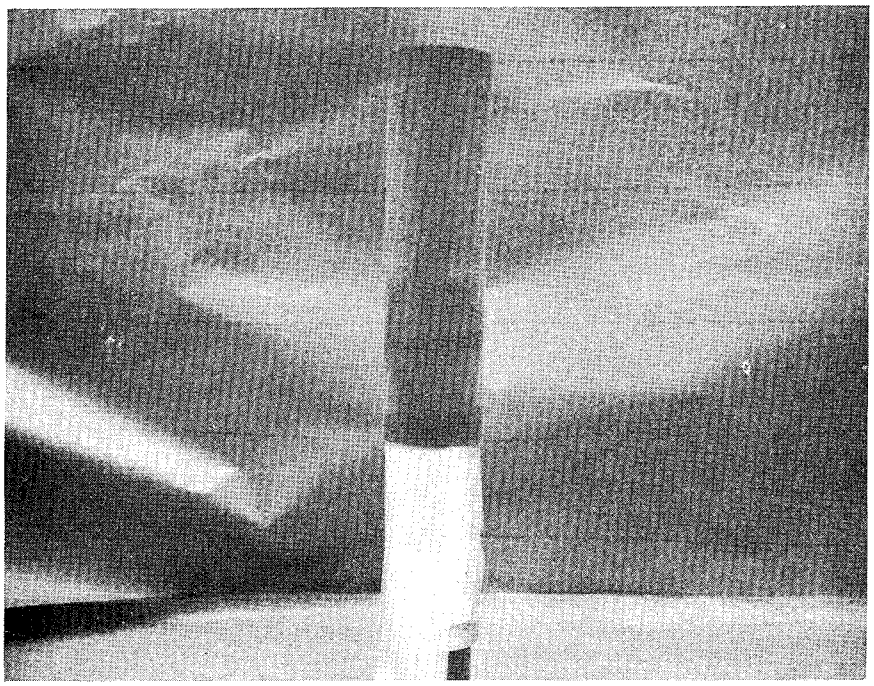


b. Mounting Preform Cylinder on Mandrel

Fig. 26 Unassembled and Partially Assembled Cylinder Curing Mandrel

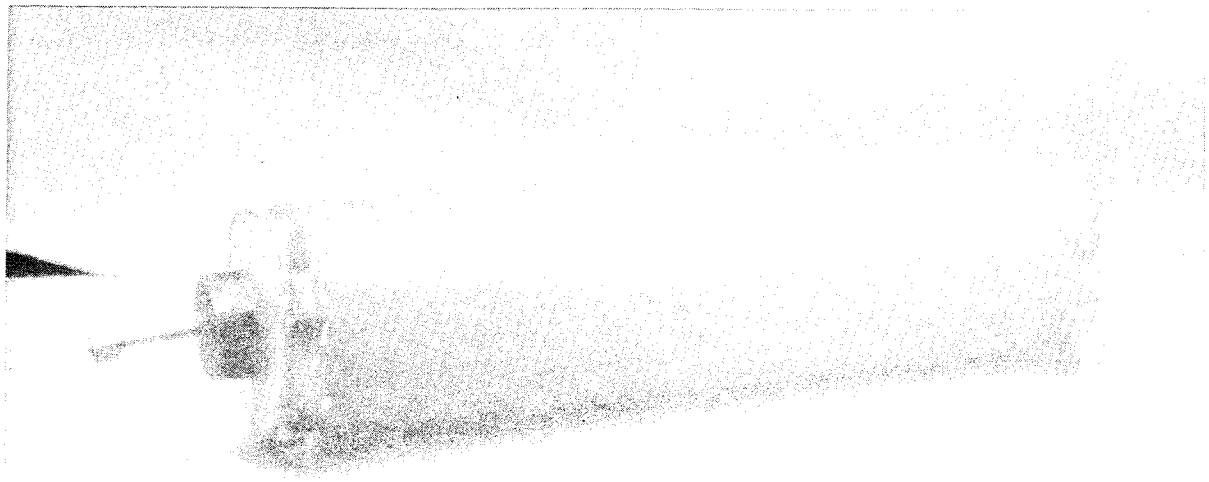


a. Wrapping Mandreled Preform Cylinder



b. Rubber Bagging Mandreled Preform Cylinder

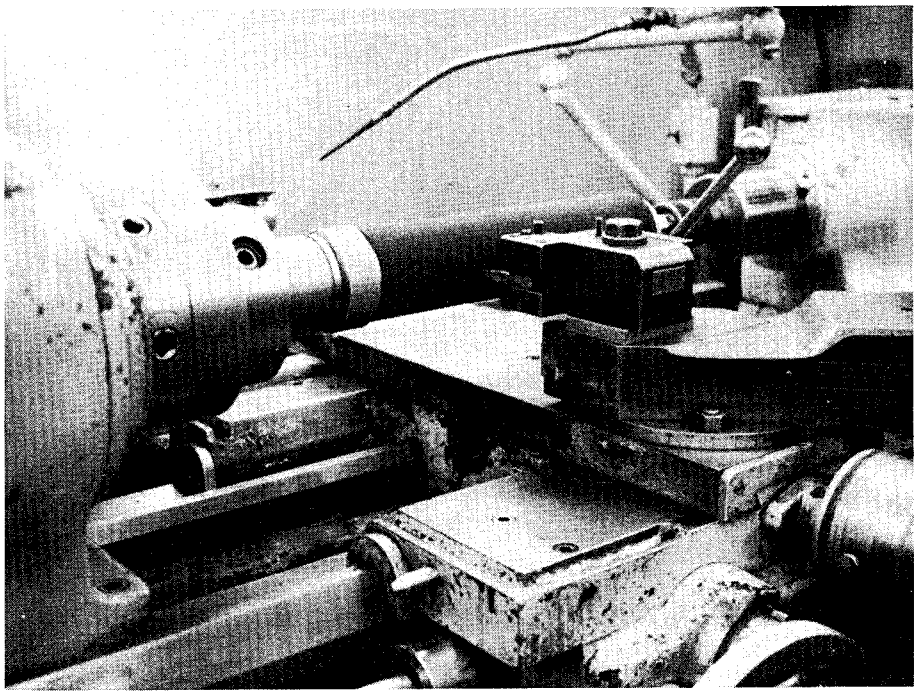
Fig. 27 Assembling Cylinder Curing Mandrel



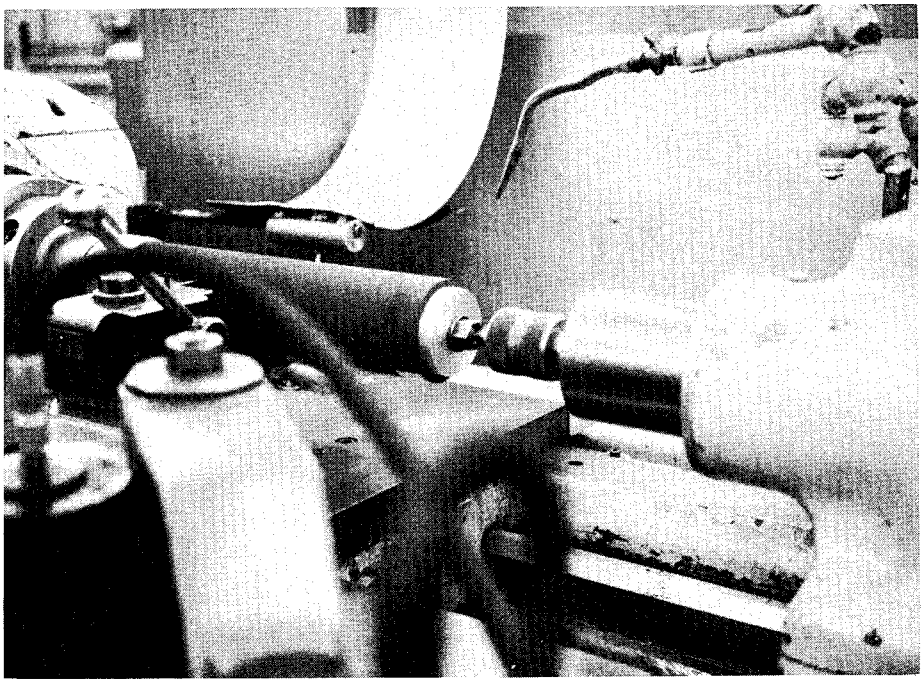
a. Cylinder Assembled for Cure

b. Machining Inside Diameter of Post Cured Cylinder

Fig. 28 Preform Cylinder, Assembled for Cure, Machining Cylinder



View "A"



View "B"

Fig. 29 Machining Outside Diameter of Post Cured Cylinder

3.3.2 Cylinders Delivered

The program called for the production and delivery of ten cylinders. The dimensions called out are shown in Fig. 23. Five contained phenolic microballoons, and five glassy carbon microballoons. The polybenzimidazole resin and carbon fiber content were the same in all ten cylinders.

In Table VIII the ten delivered cylinders are designated and listed. The dimensions of the cylinders are given as are the weight, volume, density, compressive strength, percent open cell structure, etc. The test results of the cylinders are discussed in section 3.3.3.

DELIVERED CYLINDERS

No.	Cylinder Designation	Date Deliv.	Density g/cc	% Open Cell Content or Porosity	Compressive Strength	Wt. gms.	Microballoons	O.D.	I.D.	Wall thickness	Vol. in^3	Length in.
1.	LPC-3-81	5/27/70	28.54	36.5%	2532	486	Phenolic	3.247	1.933	.657	64.60	12.093
2.	LPC-5-83	"	30.92	37.1%	2730	528	"	3.249	1.929	.660	64.90	12.075
3.	LPC-6-84	9/11/70	31.97	37.5%	2780	545	"	3.246	1.923	.662	64.78	12.067
4.	LPC-7-85	8/28/70	30.50	37.75%	2760	524.7	"	3.235	1.920	.658	63.25	12.060
5.	LPC-8-86	"	31.80	29.0%	3595	534.0	"	3.233	1.930	.652	66.77	12.077
6.	LGC-1-87	"	30.76	30.5%	3340	530.8	Glassy Carbon	3.242	1.917	.663	65.57	12.074
7.	LGC-1-88	"	30.80	30.0%	3365	522.3	"	3.240	1.918	.661	64.51	12.052
8.	LGC-2-97	"	30.56	31.1%	3330	509.7	"	3.242	1.958	.642	63.25	12.066
9.	LGC-2-98	"	31.60	35.0%	3385	524.0	"	3.240	1.956	.642	63.02	12.035
10.	LGC-3-99	9/11/70	31.74	32.0%	3820	544.0	"	3.248	1.920	.664	65.10	12.080

TABLE VIII

3.3.3 Cylinder Properties

In general the same test procedures carried out on the billets section 3.2.3 were applicable and repeated on the cylinders.

Properties relating to the chemical composition of the components, such as thermogravimetric analysis, emissivity, elemental analysis were equivalent or the same as results obtained with the billets (see section 3.2.3) and will not be discussed further.

3.3.3.1 Visual Inspection

The cylinders were initially prepared with approximately the following dimensions: 13.7" length, O.D. 3.7", and I.D. 1.9". They were then cut and machined to the size specified in Fig. 23; $12"^{+.100}_{-.000}$ length, $3"^{+.250}_{-.000}$ O.D., $2"^{+.000}_{-.100}$ I.D.

Before, during, and after the cutting and machining of the cylinders, visual inspection of the cylinders and sectioned parts was performed. Microscopic examination was also carried out. There were no apparent cracks in any of the cylinders or their parts. The cylinders were in general homogeneous in appearance.

Some of the earlier cylinders prepared did show both circumferential and vertical cracks. This cracking was corrected by changes both in the tooling as well as preform processing techniques. With these changes the problem was no longer encountered.

In general, both to visual and microscopic examination the cylinders were

homogeneous and fault free.

3.3.3.2 Compressive Strength

Compressive strength measured followed ASTM D-1621-64.

Tests were performed on specimens taken from each cylinder. Specimens were nominally 1.00" x 1.00" x 1.00" although smaller specimens were sometimes obtained due to the ring specimen dimensions from which the test specimens were cut. This did not materially affect the test results as the test specimens were accurately measured for size with a micrometer and the variance was calculated for in the final test rssults. The measurement method is described in section 3.2.3.2 were used in these tests.

The test results are shown in Table VIII, and ranged from 2532 to 3595 psi for the phenolic microballoon containing cylinder and 3330 to 3820 psi for the glassy carbon microballoon containing cylinders. These are in the accepted ranges noted in the cylinders as reported in section 3.2 .

3.3.3.3 Density

The machined billet is conditioned by heating to 350°F/2 hours, cooled in a desiccator prior to weighing and measuring the dimensions with a calipers or micrometer. If this conditioning is not performed, the tendency of the cylinders to pick up 4-6% by weight moisture from the air over a few weeks' time can cause errors in computing the density. Concomitant with the weight increase a swelling phenomenon of .6% was also noted. This can result in placing a billet out of the close dimensional specification required in Fig. 23. The overall effect of the weight and volume increase on density

however do not cancel one another out. The net effect is that the weight increase is of greater import and affects a density increase, which on a cylinder at the high end of density specification can push it over the specification requirements. These factors were first fully noted and understood on cylinders which were measured, weighed, allowed to stand, and then remeasured and reweighed prior to delivery. Placing the cylinders in an oven 350°F/2 hr returned the cylinders to their previous weight, dimensions, and density values. The density of the delivered cylinders ranged from 28.54 to 32 lb/ft^3. Of these 60% were in the range of 30 ± 1 lb/ft^3. The specified bulk density range was 30 ± 2 lb/ft^3.

3.3.3.4 Porosity, Open Cell Content

Porosity measurements were carried out using a gas technique. The method employed is described in section 3.2.3.7 as well as Appendix "B".

Table VIII tabulates the porosity or open cell content obtained for the delivered cylinders.

The test results show that the open cell content ranged for the phenolic microballoon containing cylinders from 29 - 37.7%, and 30.0 - 35.0% for the glassy carbon microballoon containing cylinders.

In the cases of the cylinders, it appears that the open cell content for the phenolic microballoon containing specimen is slightly higher than that obtained with similar density billets. In comparison the glassy carbon microballoon containing cylinders have a somewhat lower open cell content than equivalent density billets. The variances in both cases can not be explained, however they are relatively small.

4. LAMINATES

Polybenzimidazole (PBI) resin if cured and post cured at the same temperatures should ablate at equal rates. Different composite forms in which PBI is the binder, however, can demonstrate differences in ablation rate and mechanism. For this reason, a part of the ablation study to be carried out at Ames Research Center, the program called for the preparation of high density laminates constructed of carbon cloth and PBI resin. These were to be studied under ablation conditions and compared to billets and cylinder low density type composites discussed in section 3.

4.1 Components

The two components used in these laminates were Pluton B-1 HP Fabric (3M Co., St. Paul, Minn.) and Polybenzimidazole (Imidite 2801, Whittaker-Corp., Costa Mesa, Calif.) . The PBI resin is applied to the carbon cloth from a 45% solution in tetrahydrofuran.

The specifications for the fabric and PBI are in Appendix C and repeated here.

Polybenzimidazole (PBI) Imidite 2801

Whittaker Corporation, Costa Mesa, Calif.

a.	Density	spg: 1.28 - 1.32
b.	Polymer Melt Temperature	115-130°C
c.	Particle Size	50 mesh, 90% 50-200 mesh
d.	Weight Loss - (Cured PBI) @ 500°F	20% ± 2%
e.	Insolubility of PBI in (hot) H_2SO_4 after post cure	97%

Pluton B-1 HP Fabric

3 M Co., St. Paul, Minnesota

Vendor Identifying Data:

Specific gravity @ 25°C	1.86	Breaking Strength, lbs.	
Ash Content, %	9.4	warp	0.69
		fill	0.51
Finish or sizing	none		
		Filament Dia.	
Carbon content, %	83.5	in.	0.0003
Surface area, m^2/g	312	Electrical Resistance	
		ohms/sq.in.	1.7
Fabric Thickness			
in.	0.0185		
weave	square		
Yarn Count			
warp	33		
fill	32		

Elemental Composition, %

Phosphorous	1.7	Volatile Content %	7.2
Boron	2.0	Moisture Content %	5.9
Contaminant level (ppm)		Weight, oz/yd^2	6.65
Sodium	2.0		
Potassium	9		
Lithium	1		
Magnesium	3		
Calcium	8		

Analysis of the PBI resin used to prepare the laminates - Batch 92 and 93 are shown in section 3.1.1 .

The Pluton B-1 HP fabric tested gave a density of 1.85 using a Beckman Air Comparison Pycnometer. The ash content of 9.6% was obtained by carbonizing a 2 g sample in a platinum crucible using a Meker burner. The crucible was then placed in a muffle furnace at 1000°C/16 hours, cooled and reweighed. The supplier warrants the fiber to have the properties as shown above. Thermogravimetric analysis of the carbon fiber is shown in Fig. 30.

The TGA shows that the fiber contains ~6% water, starts to lose non water weight at ~ 450°C which totals 25.4% at 1000°C.

4.2 Fabrication and Processing

The fabrication and processing procedures can be found in their entirety in Appendix "C" of this report. The technique used is straight forward and follows usual procedures carried out in laminate fabrication. Other techniques,which will not be discussed herein, were carried out to prepare these laminates but were found to be inferior to the technique found in the specification.

The curing and post-curing was carried out in a continuous operation from ambient to 950°F. The curing cycle is shown on page 4 of Appendix "C". During this cycle pressure was maintained at 500 psi between 450-600°F, relieved, and reinstituted at 1000 psi between 750°-950°F. Cooling to 200°F under pressure after the post cure followed.

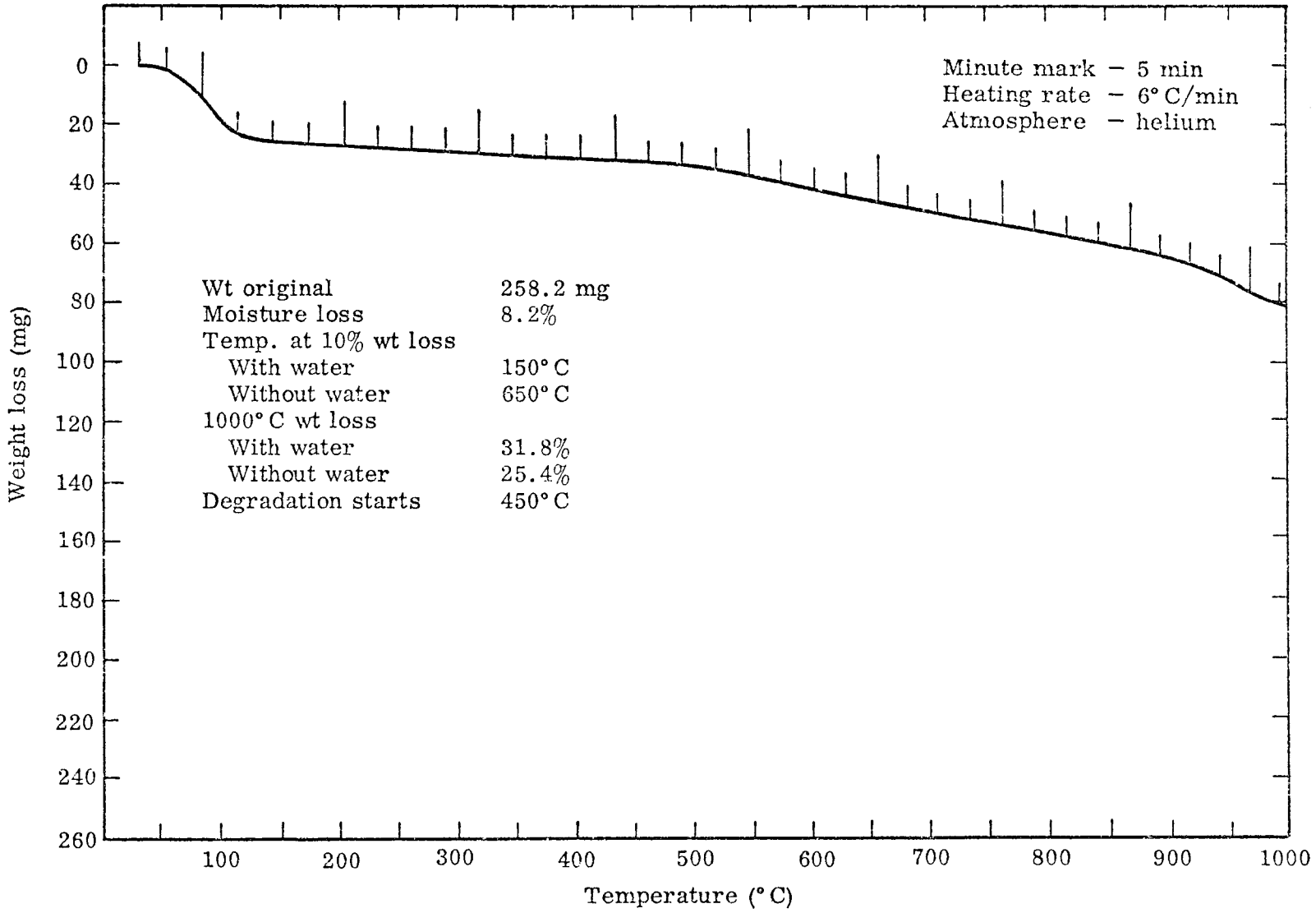


Fig. 30 Thermogravimetric Analysis of PLUTON B-1 HP (Fabric)

4.3 Laminates Delivered

The program called for the delivery of 10 laminates approximately 3/8" thick by a minimum of 5" square. In place of one of the 3/8" laminates a 1" thick one was substituted at the request of Ames Research Center. To prepare 3/8" thick required approximately 35 plies of PBI impregnated Pluton-B-1 carbon fabric. In a similar additive fashion 1" thick laminate requires approximately 92 plies.

In Table IX the ten delivered laminates are designated and listed. The dimensions of laminates are given as are density, resin content, 3 point flexural strength, number of plies, resin batch number, and Barcol hardness. The properties and tests to determine them are presented in the next section, section 4.4.

4.4 Laminate Properties and Testing

4.4.1 Flexural Testing

Flexural properties were measured by Federal Test Method 1031.1, which is a 3 point flexure test. The test calls for the maintenance of a 16:1 to 18:1 span to thickness ratio for the test sample. Unfortunately, the laminates prepared were not of sufficient length to always realize this span/thickness ratio. Indeed, the ratios measured ran from 14.5:1 to 16.2:1. The flexural strength is measured by the formula:

$$\text{Flexural Strength} = \frac{3\ (\text{Load})\ (\text{Span})}{2\ (\text{Width})(\text{Thickness})^2}$$

The nature of the laminates allowed for only two samples from the outside

LAMINATES DELIVERED

No.	Laminate Designation	Date Deliv.	Surface Dimensions in inches	Density g/cc	Resin Content	3 P.T. Flexural Strength	No. 4 Plies	Resin Batch	Thickness in.	Barcol Hardness
1	LPB 1-63	1/27/70	6.0 x 6.1	1.38	46.5%	-	36	92	.407	73
2.	LPB 1-64	1/27/70	5.9 x 6.0	1.38	44.2%	-	35	92	.383	74
3.	LPB 1-67	1/27/70	5.3 x 5.3	1.375	44.4%	10325	35	92	.395	72
4.	LPB -68	1/27/70	5.4 x 5.3	1.370	40.0%	15680	35	92	.365	72
5.	LPB -69	1/27/70	5.3 x 5.3	1.391	47.0%	13150	36	93	.408	75
6.	LPB -73	2/70	5.3 x 5.3	1.362	44.4%	13860	35	93	.398	76
7.	LPB -74	2/70	5.2 x 5.2	1.369	46.1%	22665	36	93	.407	75
8.	LPB -75	3/70	5.2 x 5.2	1.41	46.2%	10465	36	93	.396	74
9.	LPB -76	3/70	5.2 x 5.2	1.38	46.7%	20000	36	93	.406	76
10.	LPB 1-77	3/70	6.0 x 6.0	1.33	39.4	-	92	93	1.0	65

TABLE IX

edges for use in flexural testing. As a result, it was impossible to get statistical meaningful numbers. Individual results showed flexural strength ranges from 9630 psi to 23,640 psi. Table IX has the average of the two sample runs for each laminate.

All the three point flexure specimens failed as expected in bending (tension) with little to no interlaminar shear noted, as may be noted in Figs. 31 and 32.

The large variation in flexural strength 9630 to 23,640 required elucidation. Examination of the test specimens and the laminate sites from which they were cut yielded an explanation. The test samples were taken from the edges of the laminates so that the remaining pieces could be delivered to NASA as required by the contract.

Resin flow-out or lack thereof could result in starved or weaker areas near the edges which would account for the lower flexural strength. To prove this, a 5"x5" laminate IPB-1-66 with the edges removed was sectioned into nine 1/2" wide 5" long flexural test coupons. Measurements were taken of each section, with densities calculated by both weight/caliper-measurement, and weight/water displacement techniques. Flexural strength tests were then conducted following Federal Test Method 1031.1. Because of the overall size of the original laminate, the lengths of the individual test coupons were too short to fall within the "Thickness to Span" ratio called for in the Federal Test Method, thus making the resultant test values mainly of importance relative to each other.

The test values shown in Table X ranged from 23,580 psi to 28,844 psi with

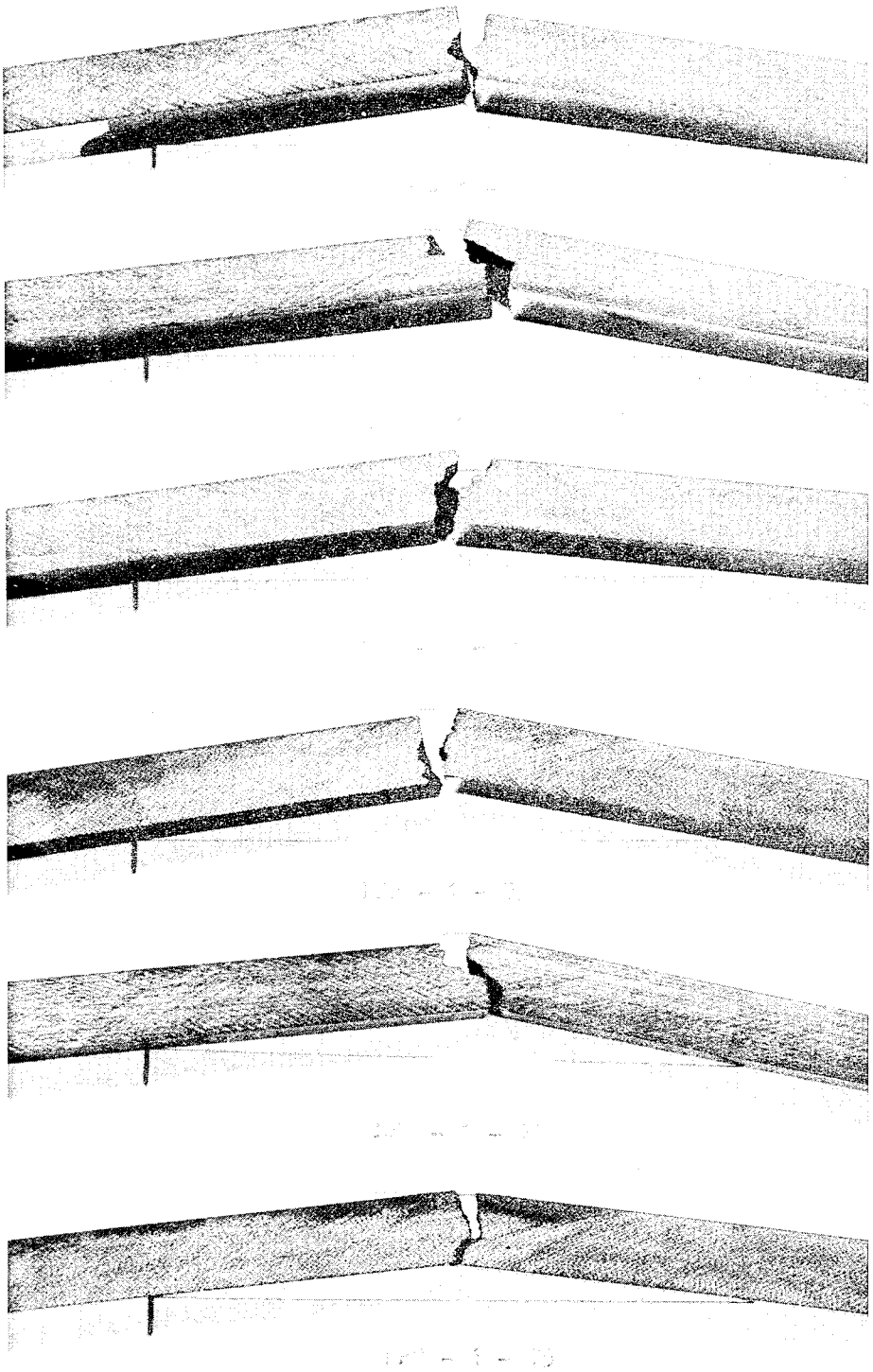


Fig. 31 3-Point Flexural Test Specimens of Designated Laminates

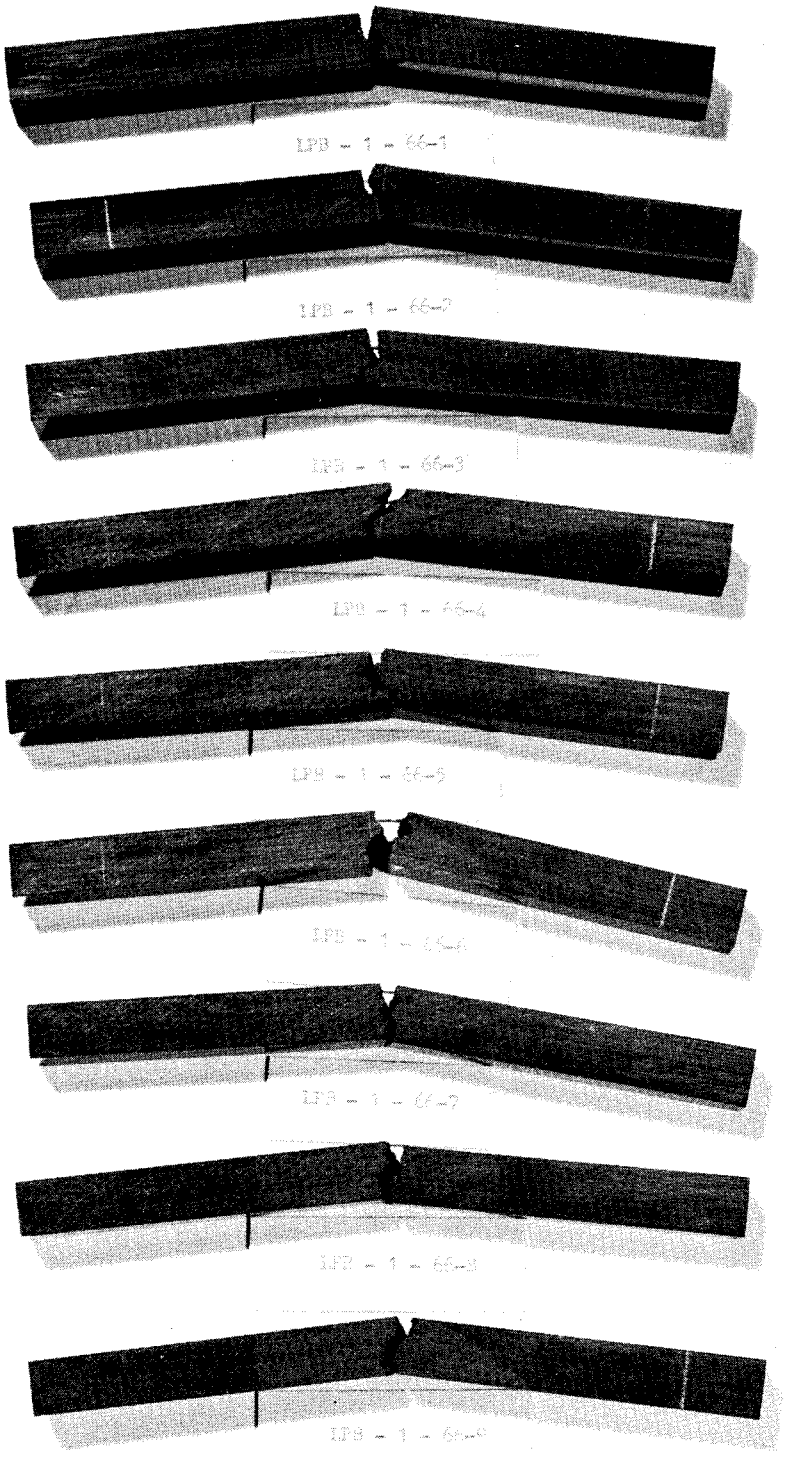


Fig. 32 3-Point Flexural Test Specimens
From Same Laminate

the greatest strength noted in the samples closest to the center. This would yield an average value of the two extremes of 26.217±2,632 psi. The average of all the values was 25,774.

The typical load-deflection curve of the three point flexure test is shown in Fig. 33 for one of the samples. The modulus of elasticity in bending for the samples ranged from 1.47 - 1.70 x 10^6 psi. It was calculated as follows:

$$E_B = \frac{L^3}{4\,bd^3}\frac{P}{Y}$$

where

E_B = modulus of elasticity

L = distance between points of support, inches

b = width of beam tested, inches

d = depth of beam tested, inches

$\frac{P}{Y}$ = slope of initial straight line portion of load deflection curve in pounds per inch of deflection.

4.4.2 Resin Content

The resin content for the laminates as seen in Table IX ranged from 39.4% to 47.0%. The method for determining these values is found in sect. 4.4.2.2 of Appendix "C".

4.4.3 Density

The density was determined by two methods. In Appendix "C" section 4.4.2.1 the method follows ASTM 1622 which accurately measures the dimensions of the laminate. The alternate method used was the water displacement technique as per ASTM D 792-64T. Using both these techniques to determine density of the

Table X

DENSITY VS FLEXURAL STRENGTH MEASUREMENTS

LPB-1-66

LPB-1-66	Length/ inches	Width/ inches	Thick./ inches	Meas. Volume cc	Dry Wt. grams	Displ. Wt/gr	Density (meas.) g/cc	Density (displ.) g/cc	Load with 4" span Lbs.	Max.* Fiber Stress PSI	E_B psix10^6	Slope P/y lbs/in of deflection
Plate	5.240	5.224	0.409	183.6	244.8	61.2	1.33	1.33				
Coupons #1	5.239	0.518	0.401	17.836	23.45	6.05	1.315	1.348	326	23,580	1.61	3360
#2	5.240	0.516	0.404	17.904	23.65	6.10	1.321	1.348	362	25,795	1.58	3360
#3	5.241	0.518	0.406	18.065	24.65	6.35	1.365	1.347	366	25,714	1.62	3520
#4	5.242	0.510	0.408	17.877	23.95	6.40	1.339	1.365	389	27,491	1.70	3680
#5	5.242	0.518	0.413	18.380	24.75	6.65	1.347	1.367	410	28,844	1.65	3760
#6	5.242	0.518	0.416	18.514	24.70	6.50	1.334	1.357	382	25,566	1.58	3680
#7	5.245	0.518	0.417	18.569	24.55	6.25	1.322	1.342	380	25,319	1.67	3910
#8	5.244	0.517	0.420	18.663	24.25	5.90	1.300	1.322	373	24,539	1.50	3600
#9	5.242	0.538	0.423	19.552	25.30	6.10	1.294	1.318	403	25,122	1.47	3760
									Avg	25,744	1.60	

* Maximum Fiber Stress = $\frac{3(\text{load})(\text{span})}{2(\text{width})(\text{thickness})^2}$

Modulus of Elasticity in Bending, $E_B = \frac{L^3}{4bd^3}\left(\frac{P}{y}\right)$

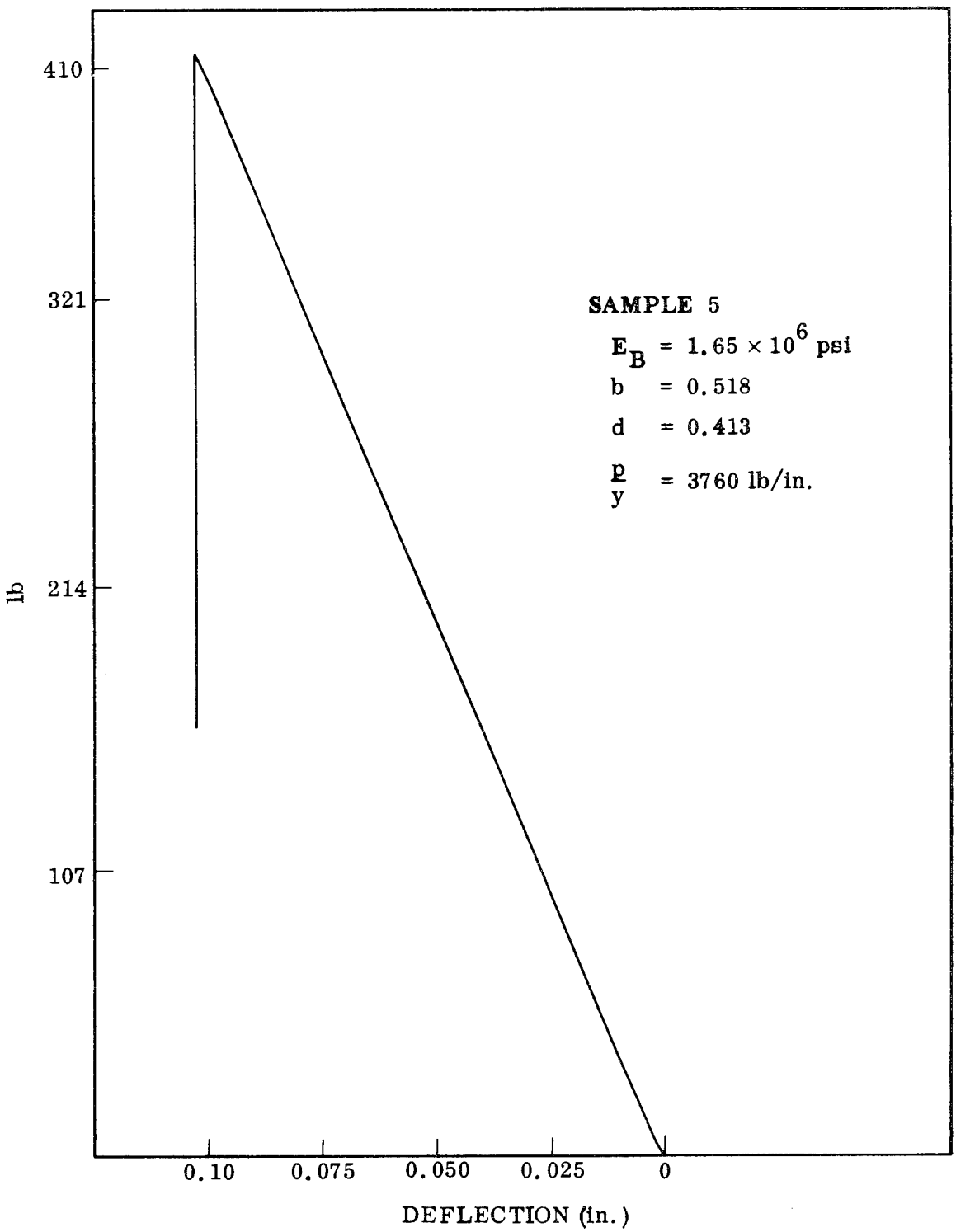


Fig. 33 3 Point Flexural Test, PBI-Carbon Cloth Laminate LPB-1-66

same specimens gave the same or very close results. The density ranged as seen in Table IX from 1.37 to 1.41 for the nine .365" to .408" thick laminates, with the 1" thick laminate at 1.33 g/cc.

4.4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of LPB-1-69 laminate is shown in Fig. 34 which shows that the ground laminate particles lose approximately 6.5% water. The total loss at 1000°F at a 5 deg. C/min. heating rate is 21%, less 6.5% water, or 14.5% loss at 1000°C. The rapid loss in weight or carbonization occurs at 650°C.

4.4.5 Barcol Hardness

The test instrument has a pointed metal indenter projecting below the base (face) of the pressure foot. When the indenter is pressed into the laminate, with the base plate resting on the laminate surface, the amount of indentation registers directly on the dial indicator.

The test measures the indentation into the laminate of the indenter under load applied by the operator, according to scale of 0-100. There is no unit of measurement. Readings taken immediately after application can vary with time due to plastic creep.

A minimum of 20 readings per specimen were made by the same operator and averaged to obtain the final reading. Care was taken to avoid indenting on carbon cloth which was in part at or very close to the surface. The Barcol hardness values shown in Table IX ranged from 72-76 for the .475" thick laminates and was 65 for the 1" thick lower density laminate.

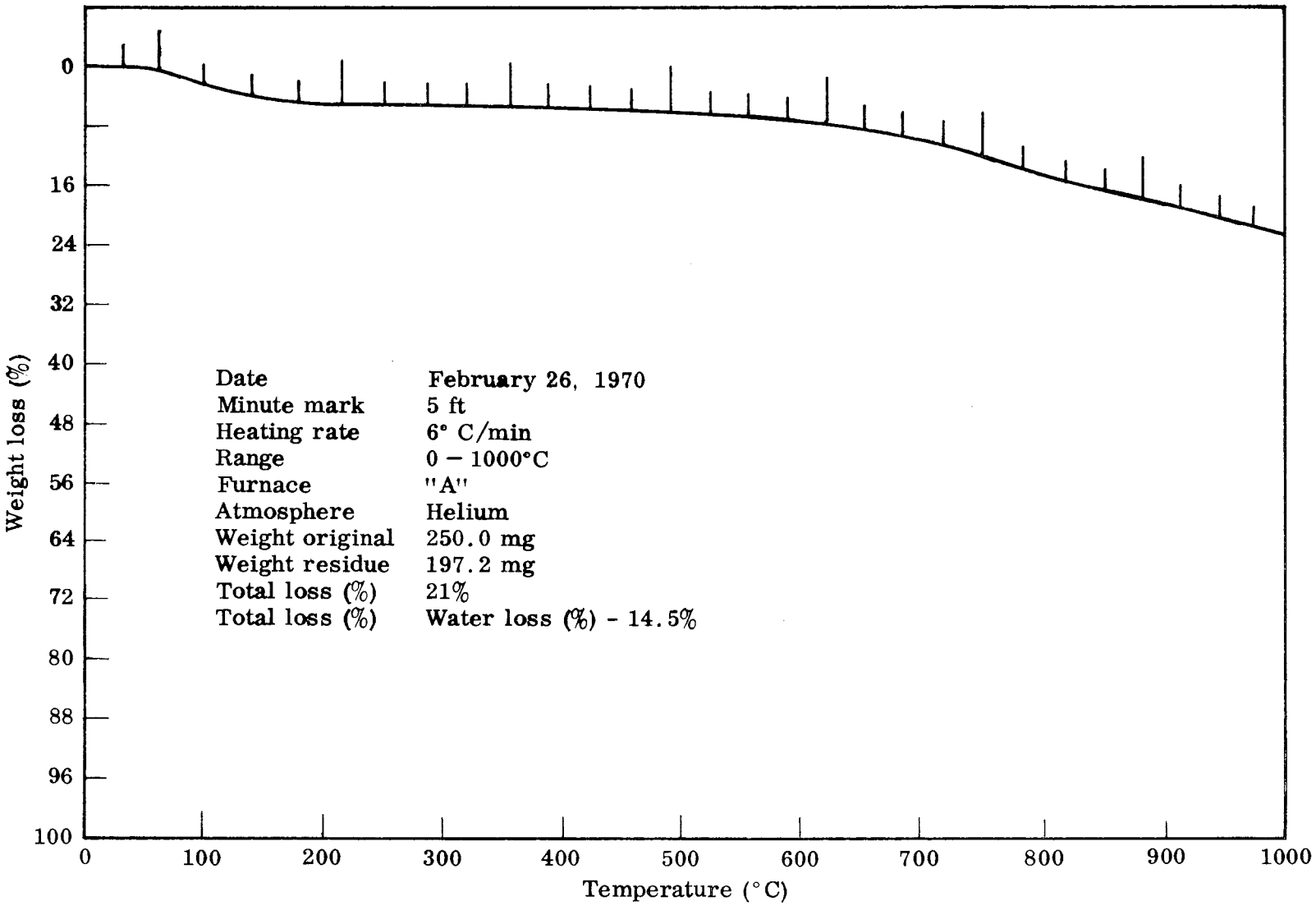


Fig. 34 Thermogravimetric Analysis of PBI LPB-1-69

Section 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

1) The processing and techniques to prepare and fabricate low density polybenzimidazole foam composites has been developed and shown to be reproducible and are documented in the included specifications. The forms developed in this program included billets and cylindrical shapes; however, other shapes should also be readily produced.

2) The properties of the 30 lb/ft^3 syntactic foam billets -- of 69% polybenzimidazole, 18% glassy carbon microballoon, and 13% chopped carbon fiber are shown in capsule form in table 11.

3) The processing and techniques to prepare and fabricate high density (1.36 - 1.41 g/cc) polybenzimidazole-carbon cloth laminates has been developed and shown to be reproducible and documented in the included specifications.

4) The high strength and superior ablative characteristics of the composites are believed to result from the high degree of thermal cross-linking obtained during the post-curing stages of the composites.

5) Preliminary ablation testing of the 30 lb/ft^3 syntactic foam billets conducted by Ames Research Center has shown the following:

a) Ablative behavior is equivalent for billets containing either glassy carbon microballoons or phenolic microballoon. The glassy carbon containing microballoon billets, however, have better mechanical properties.

Table 11

FORMULATION AND PROPERTIES OF POLYBENZIMIDAZOLE FOAM

POLYBENZIMIDAZOLE BILLET – 30 lb/ft^3

COMPOSITION	PROPERTIES
69% PBI	TENSILE – 1500 PSI
13% CARBON FIBERS	COMPRESSION 4500 PSI
18% GLASSY CARBON MICROBALLOON	THERMAL CONDUCTIVITY
	k = 0.07 Btu/ft^2 hr °F/ft
	ABLATION – LOSS 0.3"/SPACE SHUTTLE REENTRY
	MODULUS (T & C) = 1.1X10^6 PSI

b) Billets impregnated at Ames Research Center with 5 and 10% polymethyl methacrylate showed a decrease in the mass-loss of 12 to 16% during ablation testing. The following ranges of flow variables were used during the testing at the Ames Research Center's Heat Transfer Tunnel:

$$0.68 \leq P_{T_2} \leq 1.45 \text{ atm}$$

$$620 \leq q_{cw} \leq 2910 \text{ BTU/ft}^2 \text{ sec}$$

$$5300 \leq h_t \leq 1800 \text{ BTU/lb}$$

c) Billets impregnated at Ames Research Center with various amounts of polyethylene have shown reductions in surface recession rate when compared to unfilled billets. The ablation conditions used were:

Stream enthalpy: 3000 BTU/lb

Stagnation pressure: .008 atmosphere

Heat Transfer Rate: 27 BTU/ft^2

d) Films of the ablation testing of the PBI-billet samples when compared to carbon and graphite systems graphically portray the PBI billet's low thermal conductivity and the high thermal protection to be expected from these systems.

5.2 RECOMMENDATIONS

1) The degree and type of crosslinking obtained in the resin binder should be correlated with the final ablation performance. In this way, the optimum crosslinking type and density would be known.

2) The study on the effects of polymer impregnation on ablation performance of the syntactic foam composites should be continued and completed, in order to obtain the optimum transpiration system.

3) Methods of composite attachment should be investigated.

4) Lower density polybenzimidazole billets $\sim$ 15 lb/ft^3 should be prepared and studied. This would probably entail preparation of the foam in conjunction with a honeycomb structure.

5) Utilization of a 3D fiber matrix for preparation of both the low and high density polybenzimidazole composites should be examined. The 3D structure should guarantee equal strength in all planes as well as better ablation performance. The latter effect would result from long fibers which would further protect and enmesh the ablating resin system and allow for a more even divestiture of ablating gas. It would also help avoid any possible delamination and spallation problems.

6) Other research carried out under Lockheed funding has demonstrated that pyrollized PBI-billets may be coated with silicon carbide both on the surface and throughout its porosity. This new process could be used to produce a non-oxidizable reusable, radiative, heat shield which could meet Space Shuttle requirements for thermal protection. Silicon carbide is a non-permeable material which is useful in an oxidative atmosphere to 3000°F. These SiC coated systems should be prepared, investigated, and tested for Space Shuttle needs.

Section 6

REFERENCES

(1) R. R. Dickey, J. H. Lundell, and J. A. Parker, "Development of Polybenzimidazole Composites as Ablative Heat Shields", J. Macromal. Sci. - Chem., A3(4), p.573 (1969)

(2) B. Marks and L. Rubin, "Ablative Resins for Hyperthermal Environments", J. Macromal. Sci.-Chem., A3(3), pp 555 - May 1969

(3) F. B. Bahnsen, Jr., and L. E. Shoff, SAMPE 12th National Symposium, Oct. 1967, Anaheim, Calif., "Advanced in Structural Composites", Vol. 12, Western Periodicals, pg. P-1.

(4) R. H. Harding, "Determination of Average Cell Volume in Foamed Products", Mod. Plastics, 37(10), 156 (1960)

APPENDIX "A"

POLYBENZIMIDAZOLE BILLETS

SPECIFICATION & MANUFACTURING STANDARDS

SPECIFICATION

FABRICATION OF LOW DENSITY POLYBENZIMIDAZOLE BILLETS

1.0 SCOPE

1.1 Scope. This specification defines the material and fabrication requirements for syntactic polybenzimidazole (PBI) composites (billets).

1.2 Classification. Adherence to the requirements herein shall produce porous char-forming compositions having a density of 30 lbs $\pm$ 2 lbs/ft^3, suitable as heat shields for reentry of reusable space vehicles, transpiration cooling type heat shields, and heat shields for space probes.

2. Applicable Documents

American Society for Testing and Materials, ASTM D-1621-64 - Compressive Strength of Rigid Cellular Plastics.

ASTM D-1622 - Specific Gravity from Weight and Volume Measurements.

American Chemical Society, Analytical Chemistry, Vol. 19, page 925 (1947).

Blackiston Company, Philadelphia, Pa., F. Pregl "Quantitative Organic Microanalysis", page 1046.

3. Requirements

3.1 Materials and Equipment

3.1.1 Materials. Materials supplied for the fabrication of PBI composites (billets) shall be of the following designation and shall conform to the requirements stated herein.

3.1.1.1 Polybenzimidazole (PBI) Imidite 2801

Whittaker Corp.

a. Density	Spg: 1.28 - 1.32
b. Polymer Melt Temperature	115°C to 130°C
c, Particle Size	50 Mesh, 90% 50-200 Mesh
d. Weight loss (500°F cured PBI)	20% ± 2%
e. Insolubility of PBI in (hot) H_2SO_4 after post cure	98% ± 1.0%
f. Thermogravimetric Analysis to 1000°C	Weight Loss < 28%

3.1.1.2 Carbon Fibers - CCA-1

Hitco

a. Composition	95% amorphous carbon min.
b. Fiber length	1/2" Nominal
c. Volatile Content	3.0% Max.

3.1.1.3 Phenolic Microballoons - BJO-0930

Union Carbide Corp.

a. Bulk Density	0.10 - 0.12 g/cc
b. True Density	.322-.334 g/cc
c. Particle Size	< 20 mesh, 90% 50-100 mesh
d. Broken Balloons	< 3%

e. Volatile Content 8.0 % max.

3.1.1.4 Glassy Carbon Spheres, LMSC Glassy Carbon Grade 1000

Lockheed Missiles & Space Co.

a. Bulk Density .135-.165 g/cc

b. True Density .358-.370 g/cc

c. Particle Size <20 mesh, 90%, 50-100 mesh

d. Broken Balloons <3%

e. Volatile Content 3.0% max.

3.1.2 Equipment

The following major items of equipment are required for this process:

a. Weighing equipment

b. V-Blender

c. Hammer Mill

d. Forced-draft Oven

e. Hydraulic Press

f. Vacuum Pump

g. Furnace

h. Metal Molding Frames (Molding Tools)

3.2 Composition

The molding composition for preparation of ablative billets shall consist of the following:

a. Polybenzimidazole (PBI) 69% ± 0.1%

b. Carbon Fibers 13% ± 0.1%

c. Phenolic Microballoons or Glassy Carbon Spheres 18% ± 0.1%

NOTE: Conditioning of materials -
The carbon fibers, phenolic microballoons, and glassy carbon spheres shall be conditioned in a forced draft oven at 300°F ± 10°F for 3 hrs. ± 15 min. to remove volatiles prior to weighing.

3.3 Process Procedure

3.3.1 Milling and Mixing

The PBI and the carbon fibers shall be mixed in a manner which prevents fibers from forming agglomerates that cannot be dispersed or penetrated by PBI powder. The procedure for preparing the molding compound shall be as follows:

3.3.1.1 Grind the bulk fiber through a hammer mill fitted with a No. .008 screen.

3.3.1.2 Weigh the required amount of dried fiber and PBI, then mix for 20 to 25 minutes in a V-blender.

3.3.1.3 Run this mixture through a hammer mill fitted with a stainless steel 20-mesh screen (.034" opening).

3.3.1.4 Weigh the required amount of the mixture along with the required amount of dried phenolic microballoons or glassy carbon spheres, and mix in a V-blender for a minimum of 2 hrs.

3.3.1.5 After the V-blending, sieve mixture through a Tyler Standard or equivalent No. 20 screen, (.033" opening per inch).

3.3.1.6 Examine three randomly selected samples of the mixture at 35 x magnification. No agglomerates of fiber shall be present and components

shall be completely and uniformly dispersed.

3.3.2 Preforming

3.3.2.1 Four metal stops (1.220-in.) are placed on two opposite sides of the preform mold prior to packing the resin mixture (756 gram) for a one-inch billet into the preform mold. Similarly, four metal stops (2.210-in.) are placed into the preform mold prior to packing the resin mixture (1390 gram) for a two-inch billet. The square inch area for each mold shall be the same (64-sq.in.). These stops are molded into the preform to insure proper volume during cure and to obtain the required density, 30 lb $\pm$ 2 lb/ft^3 after post-cure.

3.3.2.2 Uniformly pack the required weight of mixture into the mold, and place in an oven at 250°F for 20 to 25 minutes.

3.3.2.3 Transfer the mold to a hydraulic press preheated to 250° $\pm$ 5°F, slowly apply 50 to 60 psi pressure until plug is settled on stops, hold for 20 to 25 minutes.

3.3.2.4 Allow preform to cool to 150°F before removing the mold.

3.3.3 Curing

3.3.3.1 Place two layers of asbestos sheet and two layers of silicon treated glass fabric into the curing mold. Position the preform, surrounded on all four sides and top with two layers of glass cloth and two layers of asbestos sheet; then place a 1/8-in. thick metal plate on the assembly, followed by a silicone rubber sheet diaphragm held

in place by bolting the top of the mold to the bottom, place into an air circulationg oven, connect the vacuum lines and cure according to the following schedule.

1" Billet	2" Billet
15 min. at 250°F	45 min. at 250°F
45 min. at 300°F	85 min. at 300°F
60 min. at 350°F	100 min. at 350°F
60 min. at 400°F	60 min. at 400°F
45 min. at 500°F	45 min. at 500°F
20 min. at 600°F	45 min. at 600°F

NOTE: Apply vacuum (28" to 30" Hg) when temperature reaches 350°F.

3.3.3.2 Cool under pressure to 200°F before removing billet from mold.

3.3.4. Post Curing

3.3.4.1 The cured billets are stacked between graphite plates separated by carbon fabric, thermocoupled and placed into a stainless steel drum fitted with a nitrogen purge line and adjusted to flow rate of 4 liters per minute.

3.3.4.2 Raise the furnace temperature uniformly from room temperature to 600°F ± 10°F in two (2) hours ± 15 min. Then post cure billet according to the following schedule:

600°F to 700°F	Raise at 1.0°F/min.
700°F	Hold 20 min.

700°F to 800°F	Raise at 1.0°F/min.
800°F	Hold 20 min.
800°F to 950°F	Raise at 1.0°F/min.
950°F	Hold 30 min.

3.3.4.3 Cool billet in nitrogen or argon atmosphere to 200°F before removing.

3.3.5 Composite Data

Fabricated heat shield composites shall meet the following requirements:

a. The billet shall be free of stress-cracks

b. Compressive Strength 2000 psi, min.

c. Porosity 45%

d. Homogeneity - Shall be free of material segregation and have uniform fiber distribution

e. Density 30 lbs ± 2 lb/ft^3

f. Chemical Analysis:

	Composition with Phenolic Microballoons	Composition with Glassy Carbon Beads
1. Carbon	82.85%	84.85%
2. Hydrogen	3.8%	2.95%
3. Nitrogen	10.6%	11.25%

4.0 Quality Assurance Provisions

4.1 Surveillance

Surveillance shall be maintained to assure that parts (billets) are fabricated in accordance with this specification. Unless otherwise

specified in the purchase order, the supplier is responsible for the performance of all inspection requirements so specified herein.

4.2 Classification of Tests

a. Material Inspection

b. Conformance Tests

4.3 Materials Inspection

Materials inspection shall verify that materials used for the fabrication of low density syntactic heat shields are in accordance with the requirements stated herein and materials used have been tested by the fabricator or certification has been furnished by the supplier to show that such tests have been conducted.

4.3.1 Polybenzimidazole

The following tests shall be conducted on polybenzimidazole resin:

4.3.1.1 Density

Density measurements shall be determined on a Beckman Model 930 Air Comparison Pycnometer by the Standard Operation Mode described for Atmosphere Operation 1 to 2.

4.3.1.2 Polymer Melt Temperature

Melting point temperature shall be determined on a Fisher-Johns melting point apparatus.

4.3.1.3 Particle Size

Particle size shall be determined with Tyler Standard Series or

U.S. Series equivalent. Particle size shall be less than 50 mesh, with 90% retained between 50 - 200 mesh.

4.3.1.4 Weight Loss

Weight loss determination shall be done on PBI resin in accordance with the following procedure: Two specimens of each batch shall be weighed into preconditioned (dried), preweighed, ceramic vessels and heated from room temperature to 500°F in air following the billet curing schedule. (See Paragraph 3.3.3.1). Remove from the oven after holding at 500°F for 45 min. ± 5 min., cool in a desiccator and reweigh.

4.3.1.5 Solubility of PBI in (Hot) H_2SO_4 After Post Cure

Solubility determinations shall be made on PBI resin which has completed the cure and post-cure schedules outlined in Paragraphs 3.3.3.1 and 3.3.4.2.

The following techniques shall be applied:

a. The resin shall be ground to a 20-30 mesh size, dried 1 hour ± 5 min. at 300°F ± 10°F, cooled in a desiccator, 1.0 to 2.0 g weighed into preconditioned, preweighed capped container.

b. Add 50 cc of concentrated sulfuric acid to each specimen.

c. Heat to 100°C ± 5°C and hold for one hour ± 5 min., then allow to cool to room temperature.

d. Transfer the contents of each container to preconditioned, dried and tared fritted glass filters attached to a vacuum flask. Flush the containers 4 to 5 times with an addition of 50 cc

concentrated H_2SO_4 to remove all traces of dissolved resin.

e. Wash with 200 to 250 cc of water or until filtrate is neutral.

f. Dry the filter and residue at 300°F ± 10°F for 3 hrs. ± 10 min., cool in a desiccator and weigh to determine weight of insoluble resin.

4.3.1.6 Thermogravimetric Analysis

A recording TGA (Aminco Thermo Grav) or equivalent is used in the thermal evaluation of the resin. A 250 to 260 mg sample is heated in a flowing stream of helium and its weight loss profile is recorded between room temperature and 1000°C. The temperature is programmed at 6°C rise per minute.

4.3.2 Carbon Fibers - CCA-1

The following tests shall be conducted on carbon fiber:

4.3.2.1 Composition

Certification shall be furnished by the supplier with each shipment.

4.3.2.2 Fiber Length

Fiber length shall be determined by visual examination.

4.3.2.3 Moisture Content

Moisture content shall be determined by weighing the initial specimens and heating at 300°F ± 10°F for 3 hrs. ± 15 min.

Calc.: $\frac{\text{orig.wt. - wt. after heating}}{\text{original weight}} \times 100 = \%$ volatile

4.3.3 Phenolic Microballoons and Glassy Carbon Spheres

4.3.3.1 Bulk Density

Bulk density shall be determined by loading a tared 500 cc graduate with the beads and impacting until nesting has ceased.

Calculation:

$$\text{Bulk density} = \frac{\text{Wt. of sample (g)}}{\text{Volume of Sample (cc)}} = \frac{\text{Wt. Sample}}{500} \text{ g/cc}$$

4.3.3.2 Particle Size

Particle size shall be determined using Tyler Standard Sieves or equivalent. All beads shall pass through a No. 20-mesh screen; 90% shall be retained between 50- and 100-mesh screens.

4.3.3.3 Broken Microballoons

Broken microballoons (phenolic or glassy carbon balloons) shall be determined by the following procedure: Precondition first by heating at 300°F ± 10°F for 3 hrs. ± 15 min. Weigh 100 gms of microballoons into a vessel, then flood with toluene. Apply vacuum at 28" of Hg. for 15 min. Allow to stand for 1 hour. Remove all floaters (balloons) from the toluene solution. Recover the sinkers (balloons) in toluene and dry at 300°F for 1 hour, weigh,and calculate for percent broken balloons.

$$\frac{\text{Wt. of dried microballoons}}{\text{original wt.}} \times 100 = \% \text{ broken microballoons.}$$

4.3.3.4 Moisture Content

Moisture content shall be determined in accordance with Paragraph 4.3.2.3.

4.4 Quality Conformance Inspection

Quality conformance inspection shall consist of surveillance and verification that the fabricated heat shields (billets) are in accordance with requirements specified herein.

4.4.1 Stress-Cracks

Billets shall be examined visually for stress-cracks.

4.4.2 Compressive Tests

Compressive strength tests shall be performed in accordance with ASTM-D-1621-64.

4.4.3 Porosity

Porosity measurements shall be determined by utilizing a Beckman Air Comparison Pycnometer. The sample is halved, quartered, and the true volume determined at each step. The volume fraction of open cell content is determined by:

$$O_c = \frac{V_o}{V_a} \quad \frac{V_a - V_t}{V_a}$$

V_o = open cell Volume

V_a = apparent Vol. (micrometer)

The apparent surface to volume ratios $R = \frac{S}{V}$ for samples are computed and graphed against the open cell structure values. The true open cell content of the foam corrected for open cells created by cutting is determined by extrapolating the "best fit" straight line, connecting the O_c versus R points, to $R = \frac{S}{V_a} = 0$ (the O_c axis intercept).

4.4.4 Homogeneity

Homogeneity shall be determined by photomicrographing at 100 X power and visually inspecting for uniform material distribution of the composition and lack of fiber aggregation.

4.4.5 Density

Density measurements shall be determined as per ASTM D 1622, by dimensioning the billet with a micrometer, calculating the apparent volume, and then calculating the density from the predetermined weight. Measurements shall be expressed in pounds per cubic foot.

4.4.6 Chemical Analysis

Chemical analysis of the fabricated billet shall be run to determine Carbon, Hydrogen, and Nitrogen.

A section of fabricated billet is filed down with a metal file to provide the sample for analysis. This sample is dried at 200°C under vacuum or inert gas (Argon) for 2 hours. The sample is microanalyzed for Carbon and hydrogen by the Pregl method (F. Pregl, "Quantitative Organic Microanalysis", 1046, Blakiston Co., Philadelphia) Nitrogen microanalysis is by the Dumas method (W. Kirsten, Anal. Chem. 19, 925, (1947).

APPENDIX "B"

POLYBENZIMIDAZOLE CYLINDERS

SPECIFICATION & MANUFACTURING STANDARDS

SPECIFICATION

FABRICATION OF LOW DENSITY POLYBENZIMIDAZOLE CYLINDERS

1.0 SCOPE

1.1 Scope. This specification defines the material and fabrication requirements for syntactic polybenzimidazole (PBI) composites (hollow cylinders).

1.2 Classification. Adherence to the requirements herein shall produce porous char-forming compositions having a density of 30 lbs $\pm$ 2 lbs/ft^3, suitable as heat shields for reentry of reusable space vehicles, transpiration cooling type heat shields, and heat shields for space probes.

2. Applicable Documents

American Society for Testing and Materials, ASTM D-1621-64 - Compressive Strength of Rigid Cellular Plastics.

ASTM D-1622 - Specific Gravity from Weight and Volume Measurements.

American Chemical Society, Analytical Chemistry, Vol. 19, page 925, (1947).

Blackiston Company, Philadelphia, Pa., F. Pregl, "Quantitative Organic Microanalysis", page 1046.

3.0 Requirements

3.1 Materials and Equipment

3.1.1 Materials. Materials supplied for the fabrication of PBI composites (cylinders) shall be of the following designation and shall conform to the requirements stated herein.

3.1.1.1 Polybenzimidazole (PBI) Imidite 2801

Whittaker Corporation

a. Density	Spg: 1.28 - 1.32
b. Polymer Melt Temperature	115°C to 130°C
c. Particle Size	50 Mesh, 90% 50-200 Mesh
d. Weight Loss (500°F cured PBI)	20% ± 2.0%
e. Insolubility of PBI in (hot) H_2SO_4 after post cure	98% ± 1.0%
f. Thermogravimetric Analysis to 1000°C	Weight Loss < 28%

3.1.1.2 Carbon Fibers - CCA-1

Hitco

a. Composition	95% amorphous carbon min.
b. Fiber Length	1/2" Nominal
c. Volatile Content	3.0% Max.

3.1.1.3 Phenolic Microballoons - BJO-0930

Union Carbide Corporation

a. Bulk Density	0.10 - 0.12 g/cc
b. True Density	.322 - .334 g/cc
c. Particle Size	< 20 mesh, 90% 50-100 mesh

d.	Broken Balloons	< 3%
e.	Volatile Content	3.0% max.

3.1.1.4 Glassy Carbon Spheres, LMSC Glassy Carbon Grade 1000

Lockheed Missiles & Space Company

a.	Bulk Density	.135 - .165 g/cc
b.	True Density	.358 - .370 g/cc
c.	Particle Size	< 20 mesh, 90%, 50-100 mesh
d.	Broken Balloons	< 3%
e.	Volatile Content	3.0% max.

3.1.2 Equipment

The following major items of equipment are required for this process:

a. Weighing equipment

b. V-Blender

c. Hammer Mill

d. Forced-draft Oven

e. Hydraulic Press

f. Vacuum Pump

g. Furnace

h. Metal Molding Frames (Molding Tools)

3.2 Composition

The molding composition for preparation of ablative cylinders shall consist of the following:

a.	Polybenzimidazole (PBI)	69% ± 0.1%

b. Carbon Fibers 13% ± 0.1%

c. Phenolic Microballoons or Glassy Carbon Spheres 18% ± 0.1%

NOTE: Conditioning of materials -
The carbon fibers, phenolic microballoons, and glassy carbon spheres shall be conditioned in a forced draft oven at 300˚F ± 10˚F for 3 hrs. ± 15 min. to remove volatiles prior to weighing.

3.3 Process Procedure

3.3.1 Milling and Mixing

The PBI and the carbon fibers shall be mixed in a manner which prevents fibers from forming agglomerates that cannot be dispersed or penetrated by PBI powder. The procedure for preparing the molding compound shall be as follows:

3.3.1.1 Grind the bulk fiber through a hammer mill fitted with a No. .008 screen

3.3.1.2 Weigh the required amount of dried fiber and PBI, then mix for 20 to 25 mintes in a V-blender.

3.3.1.3 Run this mixture through a hammer mill fitted with a stainless steel 20-mesh screen (.034" opening).

3.3.1.4 Weigh the required amount of the mixture along with the required amount of dried phenolic microballoons or glassy carbon spheres, and mix in a V-blender for a minimum of 2 hrs.

3.3.1.5 After the V-blending, sieve mixture through a Tyler Standard or

equivalent No. 20 screen (.033" opening per inch).

3.3.1.6 Examine three randomly selected samples of the mixture at 35 x magnification. No agglomerates of fiber shall be present and components shall be completely and uniformly dispersed.

3.3.2 Preforming

3.3.2.1 The preform mold shall be cleaned with solvent, such as Methyl Ethyl Ketone and sprayed with MS-122 Fluorocarbon release agent. The mold, Fig. 1 , is then assembled by placing the outer cylinder over the inner cylinder and the bottom piston which aligns the inner cylinder in the outer cylinder.

3.3.2.2 Small quantities of the resin mix are put into the preform mold and tamped uniformly until all of the resin mix is packed into the mold. An awareness of the relationship of weight of the resin mix to the volume in the preform mold insures a good uniform pack, and better density control along the length of the cylinder.

3.3.2.3 The top plunger is placed into the mold, and the whole assembly is put into a tube furnace and heated from inside and outside of the preform mold to 325°F and held at 325°F for 30 min. before pressure (50 psi) is applied. Total elapsed time for heating is 180 min, after which the heaters are turned off and the part allowed to cool under pressure to room temperature before removing the preform.

3.3.2.4 After the preform is removed from the mold it is weighed and density recorded, and visually inspected, prior to curing.

3.3.3. Curing

3.3.3.1 The curing mandrel, Fig. 2 , is wrapped with two layers of glass cloth treated with release agent.

3.3.3.2 The cylinder is put on the mandrel, and metal end rings positioned, and the cylinder wrapped on the outside with two layers of glass cloth; then the silicone rubber bag clamped to the end rings, (see Fig. 2), sealed with a silicon adhesive (RTV-108) and the vacuum line attached.

3.3.3.3 Curing is carried out according to the following schedule under vacuum of (26 to 28 in. of Hg):

45 min. @ 250°F

45 min. @ 300°F

60 min. @ 350°F

60 min. @ 400°F

45 min. @ 500°F

20 min. @ 600°F

3.3.3.4 After cure, the cylinder is allowed to cool, with the vacuum maintained, to room temperature before removing from the mandrel.

3.3.3.5 After removal from the mandrel the part is weighed to determine the weight loss.

3.3.4 Post Curing

3.3.4.1 The cylinder is stood on a flat piece of graphite in the furnace and a metal tube 14 in. long is placed around the plastic cylinder as a precautionary measure against the cylinder falling over.

3.3.4.2 Raise oven temperature to 600°F in 2 hr., hold at 600°F for 20 min., raise temperature at a rate of 1°F/min. to 950°F with a hold of 20 min. at 700° and 800°F with a 30 min. hold at 950°F.

3.3.4.3 The furnace is turned off and the part cooled in inert atmosphere to below 150°F before exposing the parts to the atmosphere.

3.3.4.4 After post cure the cylinders are weighed to determine weight loss during post cure.

3.3.5 Machining

3.3.5.1 The cylinder is cut to $12^{+.250}_{-.000}$ in. in length.

3.3.5.2 It is then mounted in a holding fixture as shown in Fig. 3 and placed in a lathe and the inside diameter of the cylinder bored to $2^{+.000}_{-.100}$ in.

3.3.5.3 The assembly is then removed and the cylinder mounted on the holding fixture (Fig. 3), centered on the end caps and the outside diameter turned to $3^{+.250}_{-.000}$ in.

3.3.5.4 The following data is reported: Weight in grams, volume (cubic inches), outside diameter, inside diameter, wall thickness, and density (pounds

per cubic feet).

3.3.6 Composite Data

Fabricated heat shield composites shall meet the following requirements:

a. The cylinder shall be free of stress-cracks

b. Compressive Strength 200 psi, in.

c. Porosity $< 45\%$

d. Homogeneity - Shall be free of material segregation and have uniform fiber distribution

e. Density 30 lbs $\pm$ 2 lb/ft^3

f. Chemical Analysis:

	Composition with Phenolic Microballoons	Composition with Glassy Carbon Beads
1. Carbon	82.85%	84.85%
2. Hydrogen	3.8%	2.95%
3. Nitrogen	10.6%	11.25%

4.0 Quality Assurance Provision

4.1 Surveillance

Surveillance shall be maintained to assure that parts (cylinders) are fabricated in accordance with this specification. Unless otherwise specified in the purchase order, the supplier is responsible for the performance of all inspection requirements so specified herein.

4.2 Classification of Tests

a. Material Inspection

b. Conformance Tests

4.3 Materials Inspection

Materials inspection shall verify that materials used for the fabrication of low density syntactic heat shields are in accordance with the requirements stated herein and materials used have been tested by the fabricator or certification has been furnished by the supplier to show that such tests have been conducted.

4.3.1 Polybenzimidazole

The following tests shall be conducted on polybenzimidazole resin:

4.3.1.1 Density

Density measurements shall be determined on a Beckman Model 930 Air Comparison Pycnometer by the Standard Operation Mode described for Atmosphere Operation 1 to 2.

4.3.1.2 Polymer Melt Temperature

Melting point temperature shall be determined on a Fisher-Johns melting point apparatus.

4.3.1.3 Particle Size

Particle size shall be determined with Tyler Standard Series or U.S. Series equivalent. Particle size shall be less than 50 mesh, with 90% retained between 50-200 mesh.

4.3.1.4 Weight Loss

Weight loss determination shall be done on PBI resin in accordance with the following procedure: Two specimens of each batch shall be weighed into preconditioned (dried), preweighed, ceramic vessels and heated from room temperature to 500°F in air following the cylinder curing schedule. (See Paragraph 3.3.3.3). Remove from the oven after holding at 500°F for 45 min. ± 5 min., cool in a desiccator and reweigh.

4.3.1.5 Solubility of PBI in (Hot) H_2SO_4 After Post Cure

Solubility determinations shall be made on PBI resin which has completed the cure and post-cure schedules outlined in Paragraphs 3.3.3.3 and 3.3.4.2. The following techniques shall be applied:

a. The resin shall be ground to a 20-30 mesh size, dried 1 hour ± 5 min. at 300°F ± 10°F, cooled in a desiccator, 1.0 to 2.0 g weighed into preconditioned, preweighed capped container.
b. Add 50 cc of concentrated sulfuric acid to each specimen.
c. Heat to 100°C ± 5°C and hold for one hour ± 5 min., then allow to cool to room temperature.
d. Transfer the contents of each container to preconditioned, dried and tared fritted glass filters attached to a vacuum flask. Flush the containers 4 to 5 times with an addition of 50 cc concentrated H_2SO_4 to remove all traces of dissolved resin.
e. Wash with 200 to 250 cc of water or until filtrate is neutral.
f. Dry the filter and residue at 300°F ± 10°F for 3 hrs. ± 10 min., cool in a desiccator and weigh to determine weight of insoluble resin.

4.3.1.6 Thermogravimetric Analysis

A recording TGA (Aminco Thermo Grav) or equivalent is used in the thermal evaluation of the resin. A 250 to 260 mg sample is heated in a flowing stream of helium and its weight loss profile is recorded between room temperature and 1000°C. The temperature is programmed at 6°C rise per minute.

4.3.2 Carbon Fibers - CCA-1

The following tests shall be conducted on carbon fiber:

4.3.2.1 Composition

Certification shall be furnished by the supplier with each shipment.

4.3.2.2 Fiber Length

Fiber length shall be determined by visual examination.

4.3.2.3 Moisture Content

Moisture content shall be determined by weighing the initial specimens and heating at 300°F ± 10°F for 3 hrs. ± 15 minutes.

Calculation: $\frac{\text{orig.wt. - wt. after heating}}{\text{original weight}} \times 100 = \%\ \text{volatile}$

4.3.3 Phenolic Microballoons and Glassy Carbon Spheres

4.3.3.1 Bulk Density

Bulk density shall be determined by loading a tared 500 cc graduate with the beads and impacting until nesting has ceased.

Calculation:

$$\text{Bulk Density} = \frac{\text{Wt. of sample (g)}}{\text{Volume of Sample (cc)}} = \frac{\text{Wt Sample}}{500}\ \text{g/cc}$$

4.3.3.2 Particle Size

Particle size shall be determined using Tyler Standard Sieves or equivalent. All beads shall pass through a No. 20-mesh screen; 90% shall be retained between 50- and 100-mesh screens.

4.3.3.3 Broken Microballoons

Broken microballoons (phenolic or glassy carbon balloons) shall be determined by the following procedure: Precondition first by heating at 300°F ± 10°F for 3 hrs. ± 15 min. Weigh 100 gms of microballoons into a vessel, then flood with toluene. Apply vacuum at 28" of Hg. for 15 min. Allow to stand for 1 hour. Remove all floaters (balloons) from the toluene solution. Recover the sinkers (balloons) in toluene and dry at 300°F for 1 hour, weigh, and calculate for percent broken balloons.

$$\frac{\text{Wt of dried microballoons}}{\text{original wt.}} \times 100 = \% \text{ broken microballoons}$$

4.3.3.4 Moisture Content

Moisture content shall be determined in accordance with Para. 4.3.2.3.

4.4 Quality Conformance Inspection

Quality conformance inspection shall consist of surveillance and verification that the fabricated heat shields (cylinders) are in accordance with requirements specified herein.

4.4.1 Stress-Cracks

Cylinders shall be examined visually for stress-cracks.

4.4.2 Compressive Tests

Compressive strength tests shall be performed in accordance with ASTM-D-1621-64.

4.4.3 Porosity

Porosity measurements shall be determined by utilizing a Beckman Air Comparison Pycnometer. The sample is halved, quartered, and the true volume determined at each step. The volume fraction of open cell content is determined by:

$$O_c = \frac{V_o}{Va} = \frac{V_a - V_t}{Va}$$

V_o = open cell volume

V_a = apparent Vol. (micrometer)

The apparent surface-to-volume ratios $R = \frac{S}{V_a}$ for samples are computed and graphed against the open cell structure values. The true open cell content of the foam corrected for open cells created by cutting is determined by extrapolating the "best fit" straight line, connecting the O_c versus R points, to $R = \frac{S}{Va} = 0$ (the O_c axis intercept).

4.4.4 Homogeneity

Homogeneity shall be determined by photomicrographing at 100 X power and visually inspecting for uniform material distribution of the composition and lack of fiber aggregation.

4.4.5 Density

Density measurements shall be determined as per ASTM D 1622, by dimensioning the cylinders with a micrometer, calculating the apparent volume, and then calculating the density from the predetermined weight. Measurements shall be expressed in pounds per cubic foot.

4.4.6 Chemical Analysis

Chemical analysis of the fabricated cylinder shall be run to determine Carbon, Hydrogen, and Nitrogen.

A section of fabricated cylinder is filed down with a metal file to provide the sample for analysis. This sample is dried at 200°C under vacuum or inert gas (Argon) for 2 hours. The sample is microanalyzed for Carbon and Hydrogen by the Pregl method (F. Pregl, "Quantitative Organic Microanalysis," 1946 Blakiston Co., Philadelphia). Nitrogen microanalysis is by the Dumas method (W. Kirsten, Anal. Chem. 19, 925 (1947).

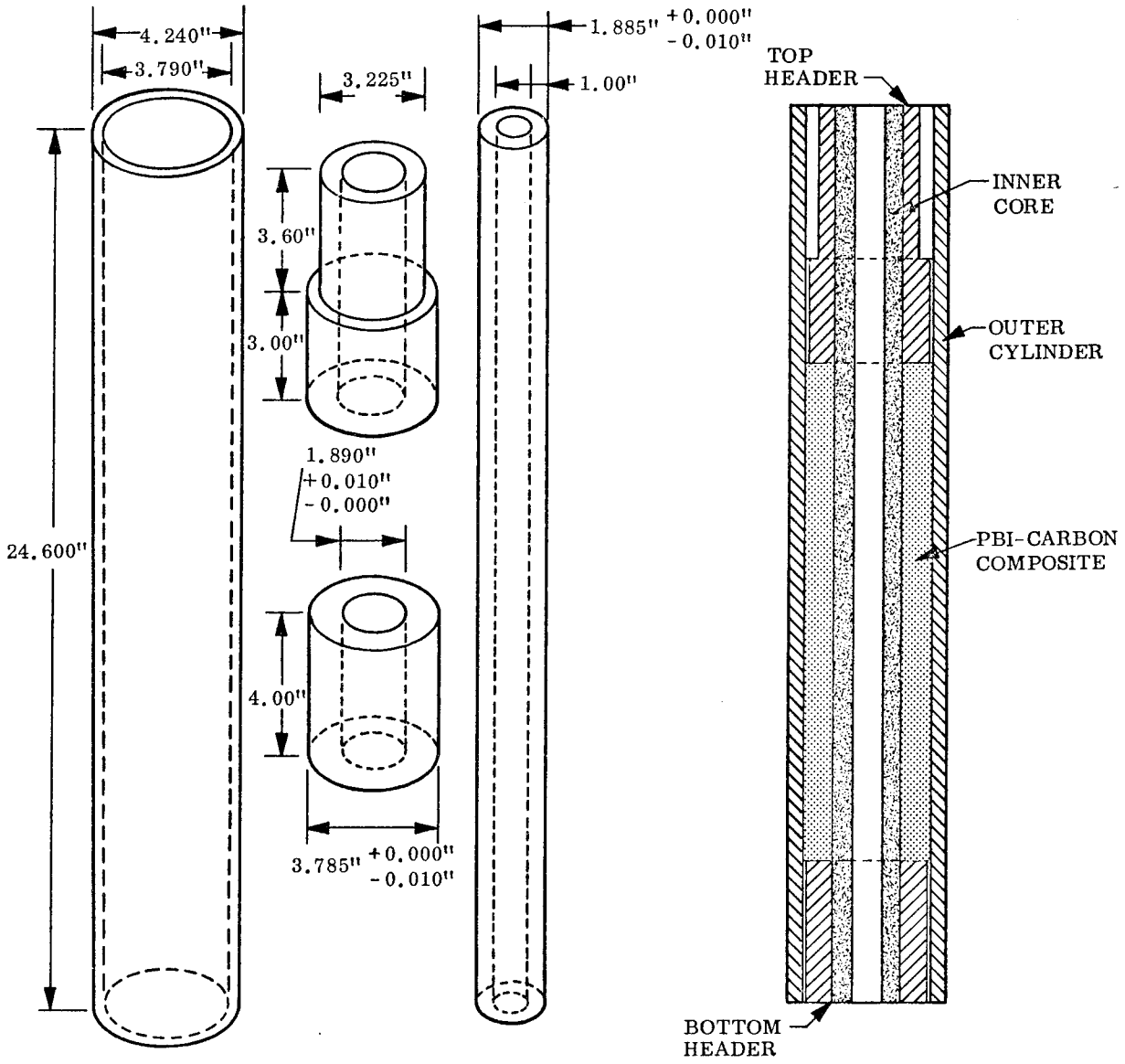


Fig. 1 Cylinder Preform Mold (Aluminum)

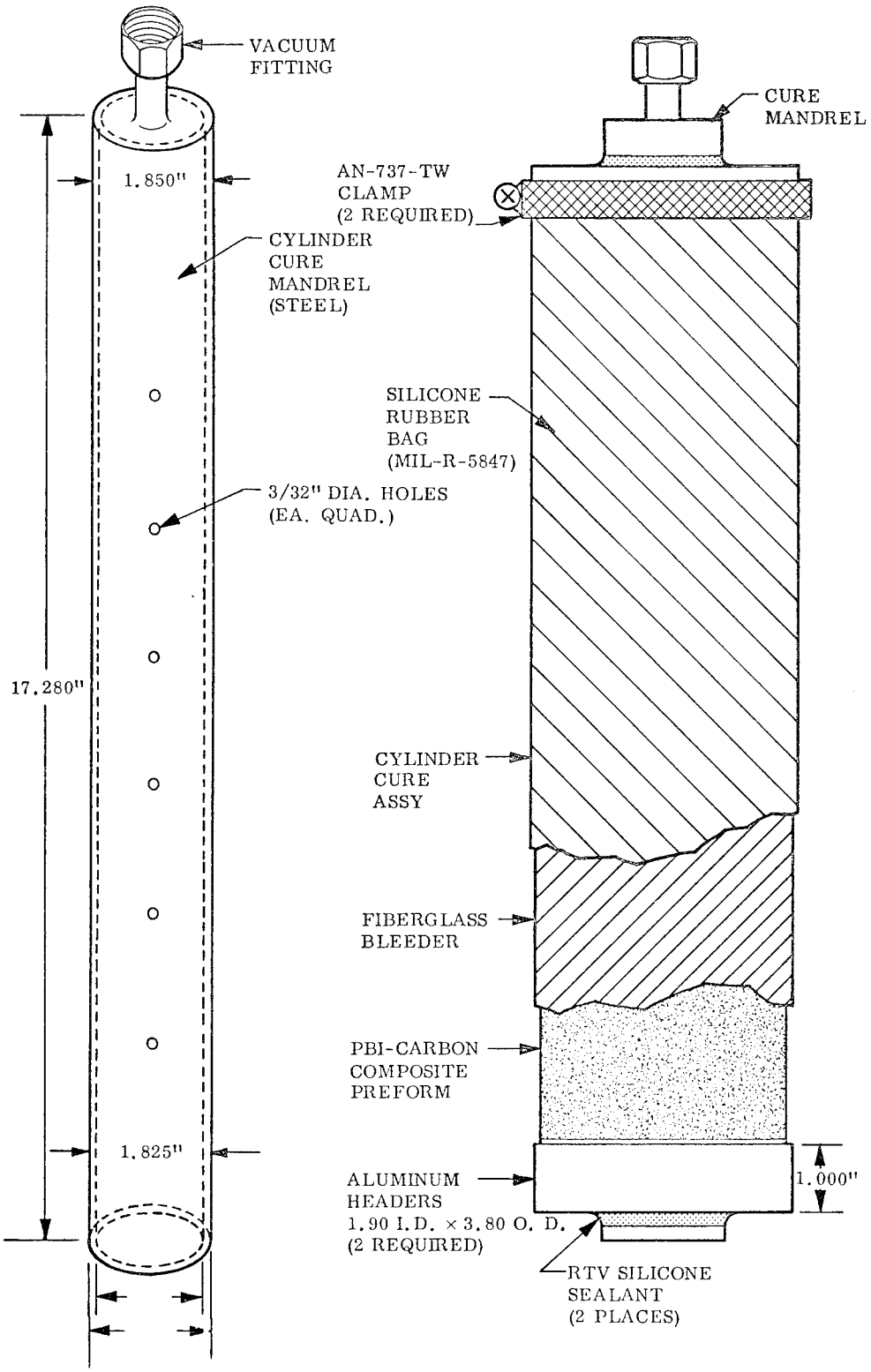
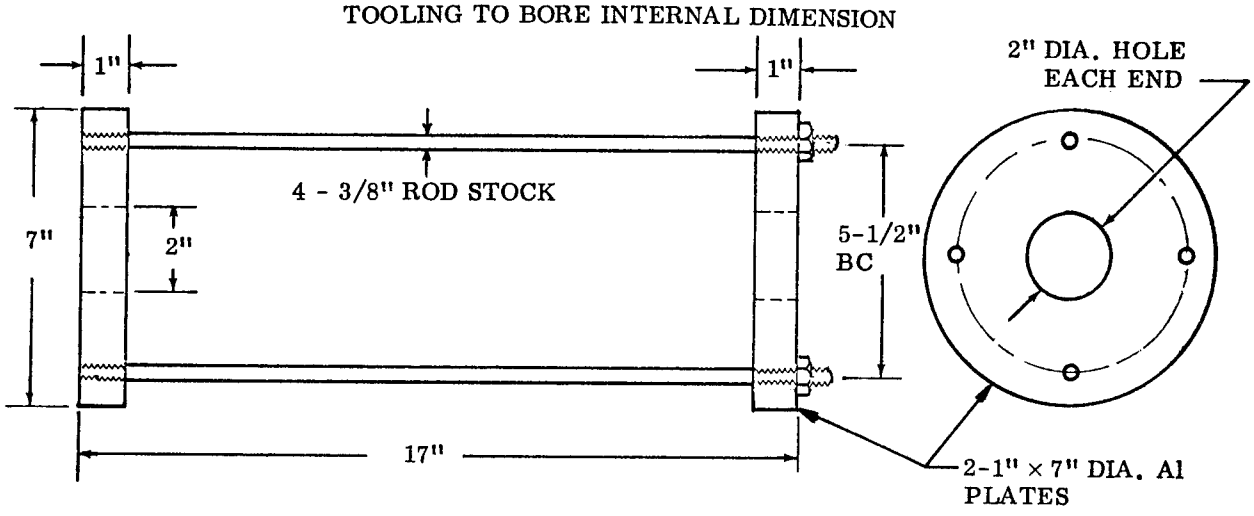


Fig. 2 Cylinder Curing Mold



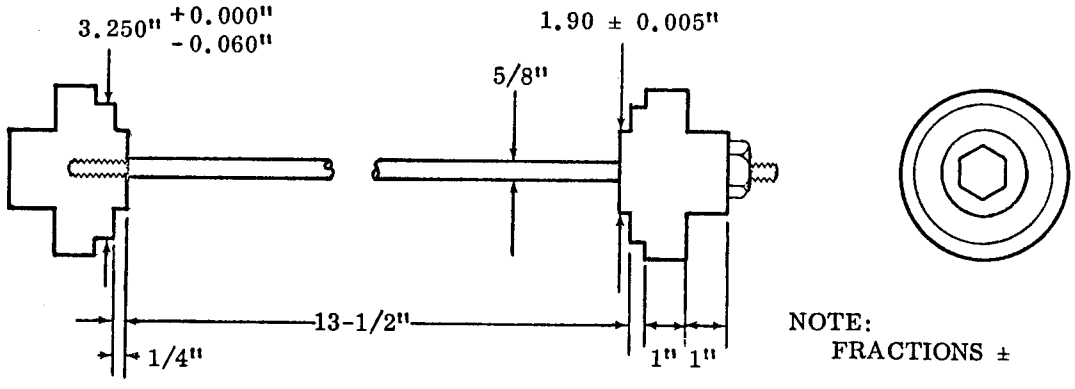


Fig. 3 Tool Layout for Machining PBI-Carbon Composite Cylinders

APPENDIX "C"

CARBON-POLYBENZIMIDAZOLE LAMINATES

SPECIFICATION & MANUFACTURING STANDARDS

SPECIFICATION

FABRICATION OF HIGH DENSITY CARBON/POLYBENZIMIDAZOLE LAMINATES (COMPOSITES)

1.0 Scope

1.1 This document defines the material and fabrication requirements for carbon/polybenzimidazole (PBI) laminates.

1.2 Classification - Adherence to the requirements herein shall produce laminates having a minimum density of 1.36 g/cc suitable as heat shields for re-entry systems.

2.0 Applicable Documents

Plastics, Organic: General Specification, Test Methods Federal Specification L-P-406, Method 1031.1

Evaluation of Selected High Performance Heat Shield Materials - BSD TR-67-127 - April 1967, p. 2-56

Beckman Instructions Manual - Model 930 Air Comparison Pycnometer - April 1965

3.0 Requirements

3.1 Materials

3.1.1 Materials - Materials supplied for the fabrication of PBI composites (laminates) shall be of the following designation and shall conform to the requirements stated herein.

3.1.1.1 Polybenzimidazole (PBI) Imidite 2801

Whittaker Corporation, Costa Mesa, Calif.

a. Density	spg: 1.28 - 1.32
b. Polymer Melt Temperature	115-130°C
c. Particle Size	50 mesh, 90% 50-200 mesh
d. Weight Loss - (Cured PBI) @ 500°F	20% ± 2%
e. Insolubility of PBI in (hot) H_2SO_4 after post cure	> 97%
f. Thermogravimetric Analysis to 1000°C	Weight Loss < 28%

3.1.1.2 Pluton B-1 HP Fabric

3 M. Co., St. Paul, Minnesota

Vendor Identifying Data:

Specific gravity @ 25°C	1.86
Ash Content, %	9.4
Finish or sizing	none
Carbon content, %	83.5
Surface area, m^2/g	312
Fabric Thickness	
in.	0.0185
weave	square
Yarn Count	
warp	33
fill	32
Breaking Strength, lbs.	
warp	0.69
fill	0.51
Filament Dia. in.	~ 0.0003
Electrical Resistance ohms/sq.in.	1.7

Elemental Composition, %			
Phosphorous	1.7	Volatile Content %	7.2
Boron	2.0	Moisture Content %	5.9
Contaminant level (ppm):		Weight, oz/yd^2	6.65
Sodium	2.0		
Potassium	9		
Lithium	1		
Magnesium	3		
Calcium	8		

3.1.1.3 Tetrahydrofuran (THF)

"Baker Analyzed" Reagents

3.2 Process Procedure

3.2.1 PBI Resin/THF Solution Mixing

Forty-five grams of PBI resin shall be added slowly to 55 grams of THF solvent. Sufficient agitation must be maintained to dissolve the resin completely.

3.2.2 Prepreg

3.2.2.1 Cut fabric to desired size and dry in an air circulating oven at 300˚F for a minimum of 30 minutes.

3.2.2.2 Roller coat a predetermined amount of resin solids uniformly on each side of the fabric.

3.2.2.3 Air dry for approximately 16 hours.

3.2.2.4 Vacuum dry (26 in. Hg) for 90 minutes at 300°F

3.2.2.5 Cut into appropriate size and weigh to determine percent resin solids of the prepreg.

3.2.3 Laminate Fabrication

3.2.3.1 Stack the required number of plies, (36 for a 0.4 in. thick laminate), in an aluminum bag, thermocouple, and roll and seal edges. Provide a fitting for a vacuum line, place bag in a platen press preheated to 300°F.

3.2.3.2 Apply contact pressure plus vacuum and cure according to the following schedule "Complete Curing Cycle of Carbon/Polybenzimidazole Laminates". (pg.C-5)

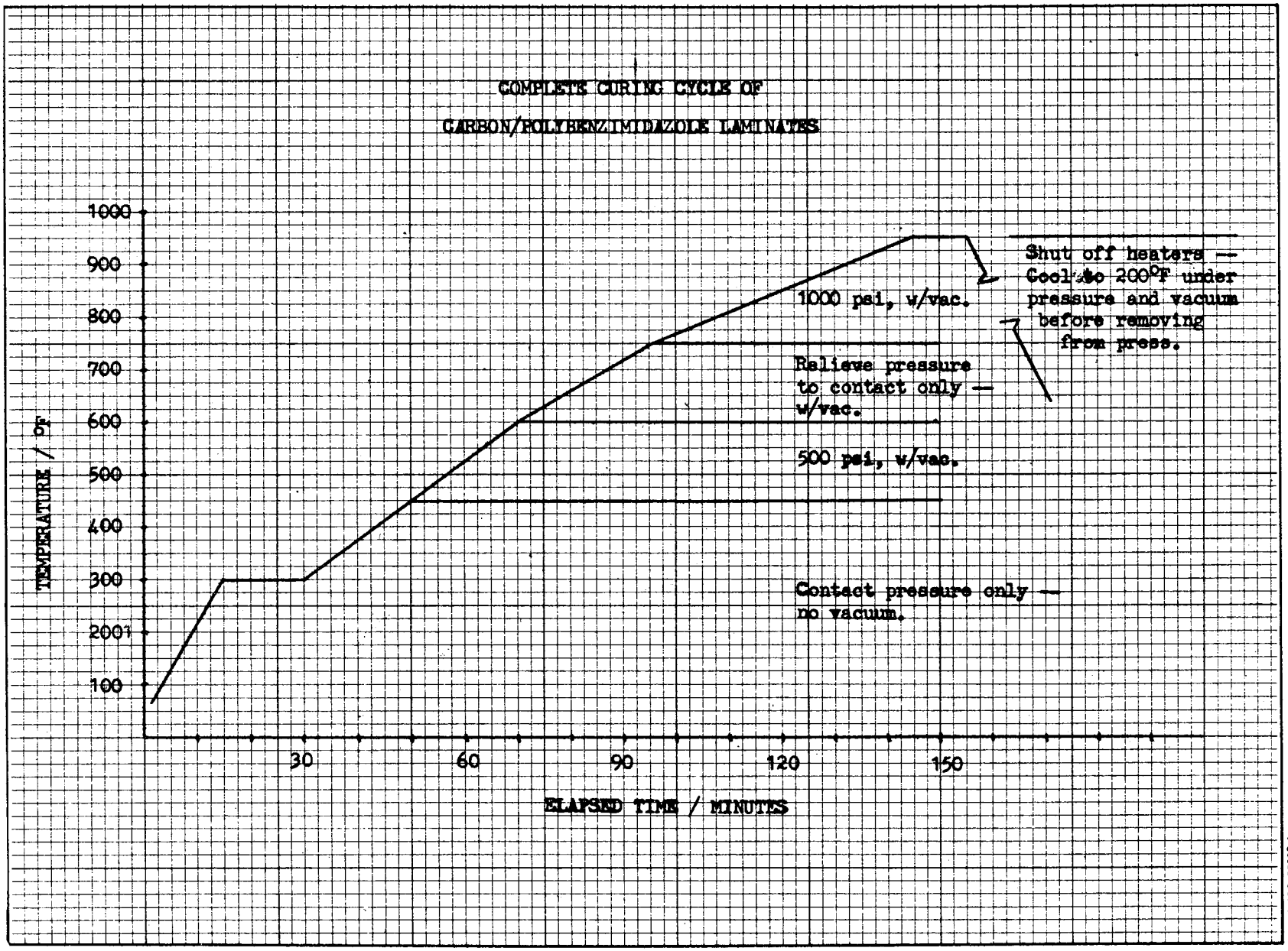
3.2.4 Pre-Preg Data

Resin content percent by wt. 55 ± 2%

3.2.5 Composite Data

Density	1.36 g/cc minimum
Resin Content	45 ± 2 percent by wt.
Barcol Hardness	60 minimum
Flexural Strength	> 10,000 psi

4.0 Quality Assurance Provisions



4.1 Surveillance

Surveillance shall be maintained to assure that the laminates (composites) are fabricated in accordance with this specification. Unless otherwise specified in the purchase order, the supplier shall be responsible for the performance of all inspection requirements so specified herein.

4.2 Classification of Tests

a. Materials Inspection

b. Conformance Tests

4.3 Materials Inspection

Materials inspection shall verify that materials used for the fabrication of carbon/PBI laminates are in accordance with the requirements stated herein and materials used have been tested by the fabricator or certification has been furnished by the supplier to show that such tests have been conducted.

4.3.1 Polybenzimidazole

The following tests shall be conducted on the polybenzimidazole resin:

4.3.1.1 Density

Density measurements shall be determined on a Beckman Model 930 air comparison pycnometer by the Standard Operation Mode described for Atmosphere Operation 1 to 2.

4.3.1.2 Polymer Melt Temperature

Melting point temperature shall be determined on a Fisher-Johns melting point apparatus.

4.3.1.3 Particle Size

Particle size shall be determined with Tyler Standard Series or U.S. Series equivalent - Screens. Particle size shall be less than 50 mesh, with 90 percent retained between 50-200 mesh.

4.3.1.4 Weight Loss

Weight loss determination shall be done on PBI resin in accordance with the following procedure: Two specimens of each batch shall be weighed into preconditioned (dried), preweighed, ceramic vessels and heated from room temperature to 950°F in inert atmosphere following the laminate curing schedule. See paragraph 3.2.3.2 excluding pressure. Remove from oven and cool in desiccator and reweigh. Weight loss is the difference between initial and final weighing.

4.3.1.5 Solubility of PBI in (hot) Sulfuric Acid After Post Cure

Solubility determination shall be made on cured PBI resin.

The following techniques shall be applied:

a) The resin shall be ground to a 20-30 mesh size; dried 1 hour ± 5 min. at 300°F ± 10°F; cooled in a desiccator; 1 to 2 grams weighed into a preconditioned,preweighed, capped container.

b) Add 50 cc of concentrated sulfuric acid to each specimen.

c) Heat to 100°C ± 5°C and hold for one hour ± 5 min., then

allow to cool to room temperature.

d) Transfer the contents of each container to preconditioned, dried and tared fritted glass filters attached to a vacuum flask. Flush the containers 4 to 5 times with an addition of 50 cc concentrated sulfuric acid to remove all trace of dissolved resin.

e) Wash with 200 to 250 cc of water or until the filtrate is neutral.

f) Dry the filter and residue at 300°F ± 10°F for 3 hours ± 10 min., cool in a desiccator and weigh to determine weight of insoluble resin.

g) Calculation: $\frac{W_2}{W_1} \times 100$ = percent insoluble resin

where W_1 = initial weight of cured resin

W_2 = weight of resin after test.

4.3.1.6 Thermogravimetric Analysis

A recording TGA (Aminco Thermo Grav) or equivalent is used in the thermal evaluation of the resin. A 250 to 260 mg sample is heated in a flowing stream of helium and its weight loss profile is recorded between room temperature and 1000°C. The temperature is programmed at 6°C rise per minute.

4.3.2 Pluton Bl-HP Carbon Fabric

The following tests shall be conducted on the carbon fabric:

4.3.2.1 Composition

Certification shall be furnished by the supplier with each shipment.

4.3.2.2 Moisture Content

Moisture content shall be determined by weighing the initial fabric (4 in. x 4 in. squares) and heating at 300°F ± 10°F for 3 hours ± 15 mins.

Calculation: $\frac{\text{original weight - weight after heating}}{\text{original weight}} \times 100$

= percent moisture.

4.3.3 Tetrahydrofuran "Baker Analyzed" Reagent

4.4 Inspection

Quality conformance inspection shall consist of surveillance and verification that the fabricated laminates are in accordance with requirements specified herein.

4.4.1 Prepreg Analysis

The resin content of the prepreg shall be determined by weight differential.

$= \frac{\text{Weight of coated fabric (total wt.) - weight of fabric}}{\text{total weight}} \times 100$

4.4.2 Laminate Analysis

4.4.2.1 Density

Density measurements shall be determined as per ASTM 1622, by dimensioning the laminate with a micrometer, calculating the apparent volume, and then calculating the density from the predetermined weight. Density to be expressed in grams per cubic centimeter.

4.4.2.2 Resin Content Determination

The resin content of a cured laminate shall be determined by differential weighing during fabrication of the laminate. The reinforcement (fabric) is preconditioned and weighed to determine weight (grams) per square inch. After lamination, cure, and final post cure, the room temperature-cooled composite is weighed. The resin content is calculated as follows:

$$\text{percent resin by weight} = \frac{W_2 - W_1}{W_2} \times 100$$

where W_2 = weight of final composite (g)

W_1 = weight of reinforcement (g)

4.4.2.3 Hardness Determination - Barcol Method (Composites)

The cured composite is tested for its hardness (average of ten readings) with a portable Barker-Coleman impressor which gives direct readings in terms of the Barcol scale. The principle relies on the force necessary to indent the surface of the specimen with a hardened steel indentor. The scale is calibrated in terms of hardness derived from various aluminum alloys of specified tempers.

4.4.2.4 Flexural Strength

Flexural strength of the laminate shall be determined in accordance with Federal Specification L-P-406, Method 1031.1, "Flexural Properties of Plastics," with the exception that the span to thickness ratio may be as low as 14:1. Test specimens, at least 1/2 in. in width shall be cut from opposite sides of the trimmed panel. Trim to be 3/4 in. on all sides.

4.4.2.5 Thermal Analysis - Thermogravimetry

(Cured Resin, Reinforcements and Composites)

A recording TGA (Aminco Thermo Grav) or equivalent is used in the preliminary thermal evaluation of the material. A 250 to 260 mg sample is heated in a flowing stream of helium and its weight loss profile is recorded between room temperature and 1000°C. The temperature is programmed at 6°C rise per minute.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546