FOREWORD

This volume is the ninth of the WADD Technical Report 61-72 series describing various phases of research and development on advanced graphite materials conducted by National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33 (616)-6915.

The work covered in this report was conducted from September 1960 through December 1962 at the Advanced Materials Laboratory of National Carbon Company, Lawrenceburg, Tennessee, under the management of R. M. Bushong, Director of the Advanced Materials Project, and of R. C. Stroup, Manager of the Advanced Materials Laboratory.

The contract for this R & D program was initiated under Project No. 7350, "Refractory Inorganic Nonmetallic Materials," Task No. 735002, "Refractory Inorganic Nonmetallic Materials: Graphitic," Project No. 7381, "Materials Application," Task No. 738102, "Materials Processes," and Project No. 7-817, "Process Development for Graphite Materials." The work was administrated by the Air Force Materials Laboratory, Research and Technology Division, Major R. H. Wilson, L. J. Conlon, and W. P. Conrardy acting as Project Engineers.

Other volumes in this WADD Technical Report 61-72 series are:

Volume I - Observations by Electron Microscopy of Dislocations Graphite, by R. Sprague.

Volume II - Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.

Volume III - Decorations of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.

Volume IV - Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.

Volume V - Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.

Volume VI - Creep of Carbons and Graphites in Flexure at High Temperature, by E. J. Seldin.

Volume VII - High Density Recrystallized Graphite by Hot-Forming, by E. A. Neel, A. A. Kellar, K. J. Zeitsch.

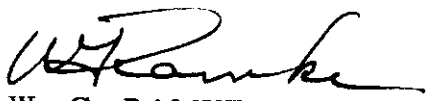
Supplement - High Density Recrystallized Graphite by Hot-Forming, by G. L. Rowe and M. B. Carter.

Volume VIII - Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner.

ABSTRACT

This report describes the development of fibrous, carbonaceous composites and laminates. Graphite, carbon, and heat-treated cloth and graphite and carbon felts are evaluated as fillers. Physical properties of the carbonized and graphitized forms of these materials are tabulated. Test results of these materials as potential hardware components are presented.

This report has been reviewed and is approved.



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1. INTRODUCTION

Full utilization of the desirable high temperature properties of graphite for aerospace applications is sometimes restricted by the brittle behavior of the commonly available grades. Recent technology has made available flexible fibers of carbon and graphite in both woven and non-woven forms. These materials have been extensively evaluated by numerous investigators as reinforcing fillers in a variety of resin bodies; however, the resin remained in a cured and unpyrolyzed state in most cases. This report summarizes a program to develop, fabricate and characterize a family of thermally-stable fibrous composites for use in high temperature thermal protection systems.

The fibrous materials employed in this study were those available commercially from National Carbon Company. Woven forms of cloth, partially carbonized, fully carbonized, and graphitized, were evaluated as fillers. Although special emphasis was placed upon evaluating the woven materials (cloth) as fillers for fibrous composites, non-woven forms of carbon and graphite felts also received limited investigation.

The individual graphite fibers in woven fabrics have tensile strengths as high as 100,000 lbs/in^2 at room temperature, and 200,000 lbs/in^2 at 2500°C.[4] Their bulk density is in the 1.5 to 1.8 g/cc range. As shown in Figure 1, these properties give the graphite fiber a strength-to-weight ratio which far surpasses that of other refractory materials at temperatures above 1000°C.

The cloth or felt can be laminated in sheet form with a resinous binder, or it can be macerated, or chopped before incorporation with the binder. The present study is concerned primarily with an evaluation of the macerated- and laminated-carbon-cloth and/or graphite-cloth-resin systems.

Macerated composites are made from fabrics which have been completely reduced to a fibrous mass by shredding or chopping, mixed with a catalyzed resin binder, and cured under pressure to a solid form. Chopped structures are fabricated from diced pieces of cloth or felt which are treated with the catalyzed binder and cured under pressure. Laminated structures are formed from sheets of resin-coated cloth stacked into multi-layers and cured under pressure. Utilization of

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these fabrication techniques along with variations in the processing temperature of the filler and of the fabricated article has yielded a family of materials designated as "PT" graphites; each material has been assigned a numerical grade (e.g., PT-0113) representing the processing involved.

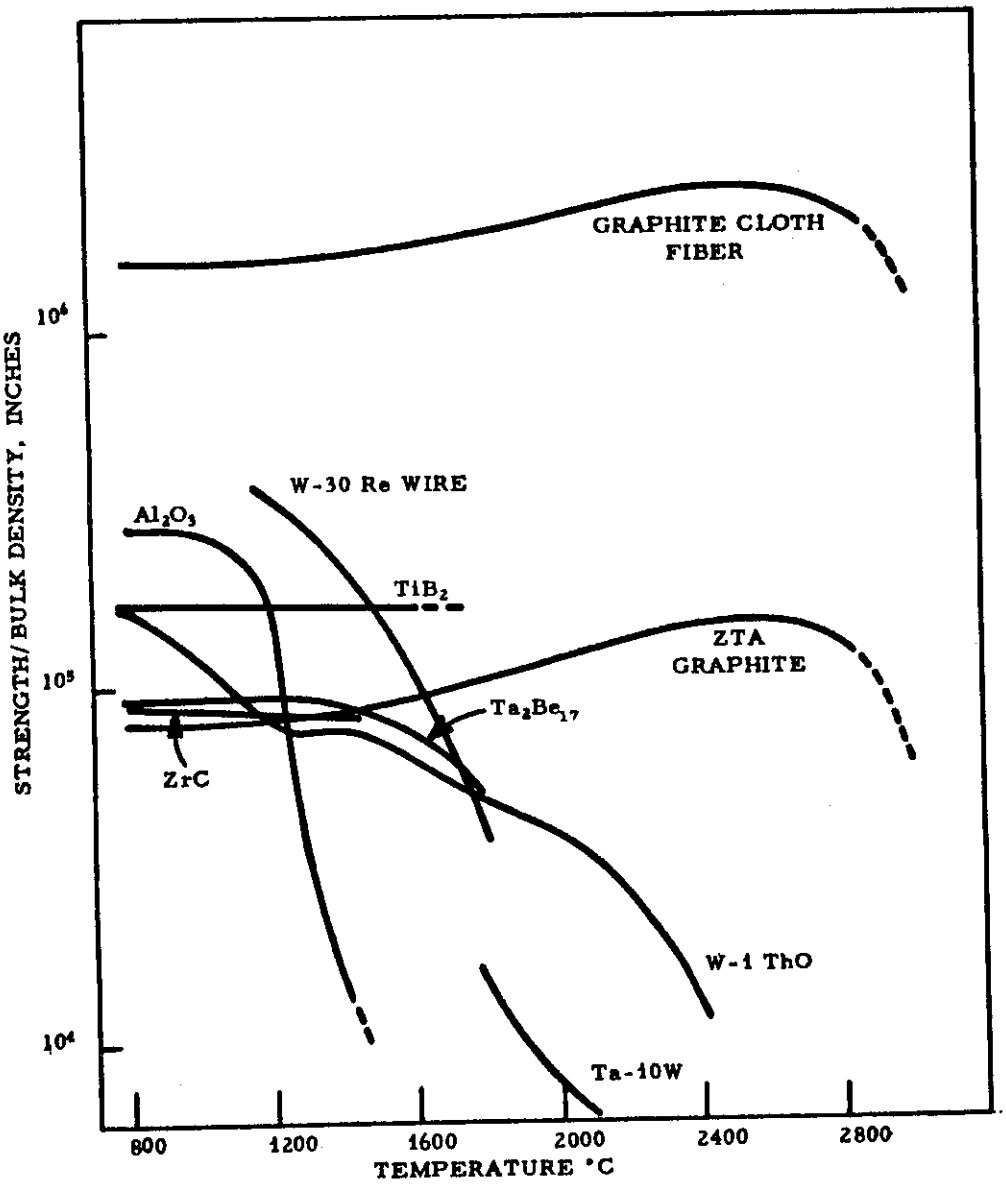

Figure 1. Tensile Strength-to-Weight Ratio for Various Materials versus Temperature

2. GRAPHITE-CLOTH COMPOSITES

Graphite cloth was the first flexible carbonaceous form to be evaluated as a filler for fibrous materials. Two basic types of resin-graphite-cloth structures were investigated, namely, those prepared from macerated cloth and those laminated from sheets of cloth. Typical of materials fabricated from a binder and a filler, structurally sound graphite-cloth composites and laminates depend upon combining these two components in the proper ratio. This ratio, called the resin-to-fiber ratio or binder level, must be high enough to bond the fiber adequately but must not exceed a point above which flaws or stresses will occur during subsequent baking and graphitizing of the fabricated article. The mechanical pressure necessary to place the fibers in suitable contact, and the weave structure and strength of the filler employed are also of importance.

2.1. Macerated-Graphite-Cloth Composites

Macerated-graphite-cloth composites are fabricated from mixtures of resin and shredded graphite cloth. These mixtures are prepared by spreading a predetermined quantity of resin over the graphite cloth, charging the resin treated cloth into a mixer and macerating the charge to a fibrous mass. The macerated material is then molded to the desired shape and cured under pressure and temperature into a solid form. The plug may then be baked and graphitized to yield a thermally-stable graphitic body.

2.1.1. Initial Studies, Macerated-Graphite-Cloth Composites

The initial studies on the fabrication and characterization of macerated-graphite-cloth composites were performed on existing equipment which could be made available for this development work. Size of the samples which could be produced with this equipment was limited; therefore, plugs used as a basis for the selection of binder level and forming pressure were too small to permit complete physical property evaluation. Selection of the initial binder level and forming pressure were based on abbreviated methods which had proved effective in predicting optimum conditions for other carbonaceous fillers.

2.1.1.1. Selection of Binder Level and Forming Pressure

The initial selection of a suitable binder level for macerated-graphite-cloth composites was based on a method outlined by Norton. [1] In a modified form, this method has been effective in predicting the optimum binder level for a carbon-flour and particle mix. The binder

level study was made of plugs 3 inches in diameter by 3 inches in height formed from mixtures of graphite cloth and a furane-phenolic resin and prepared at binder levels of 35, 50 and 70 parts of resin per hundred parts by weight of graphite cloth. The mixtures were molded at 600 lbs/in^2 by means of a hand-operated bench press and cured under pressure for 3 hours at a temperature of 120°C attained by conduction from electrically heated platens. Based on the kerosene apparent density of the graphite cloth and specific gravity of the resin, the desirable bulk density range for these plugs was selected, and the appropriate binder level of 50 parts per hundred was established.

The hand-operated press was also used in selecting a workable forming-pressure. A mixture of macerated-graphite-cloth and resin was prepared at a binder level of 50 parts per hundred by weight. This mixture was formed into plugs, 3 inches in diameter by 3 inches in height, at pressures of 200, 400, 600, 1000 and 1500 lbs/in^2. The plugs were packed in coke, baked to 800°C, and graphitized to 2800°C. Bulk density, weight loss, and shrinkage, calculated for the various heat-treatment stages, are shown in Table 1. The plug formed at 1000 lbs/in^2

Table 1. Selection of Forming Pressure for Macerated-Graphite-Cloth* Composites

Forming Pressure Lbs/in^2	200			400			600			1000			1500		
Processing Temperature °C	120	800	2800	120	800	2800	120	800	2800	120	800	2800	120	800	2800
Bulk Density g/cc	1.21	1.05	1.02	1.28	1.07	1.09	1.34	1.10	1.10	1.33	1.11	1.12	1.34	1.13	1.12
Shrinkage Per Cent															
** W.G.		1.1	0.20		1.1	0.28		1.1	0.11		1.2	0.13		0.9	0.23
*** A.G.		3.6	0.43		3.1	2.2		2.4	1.7		-2.3	0.23		1.6	0.29
Weight-Loss Per Cent		20.4	0.83		21.1	0.90		21.5	0.85		19.6	2.5		18.9	0.80

* Grade WCA Graphite Cloth
** W. G. With the grain
*** A. G. Across the grain

showed minor cracks which appeared after baking and account for the across-the-grain expansion during baking. Since the plug formed at 1500 lbs/in^2 showed no evidence of cracking, it was concluded that the plug formed at 1000 lbs/in^2 was insufficiently cured. In Figure 2, the bulk densities of these plugs plotted as a function of forming pressure at the various stages of processing, show that no appreciable density change occurred at forming pressures above 600 lbs/in^2. Therefore, a gross difference in properties would not be expected at forming pressures between 600 and 1000 lbs/in^2 but additional property measurement would be necessary to establish an optimum molding pressure.

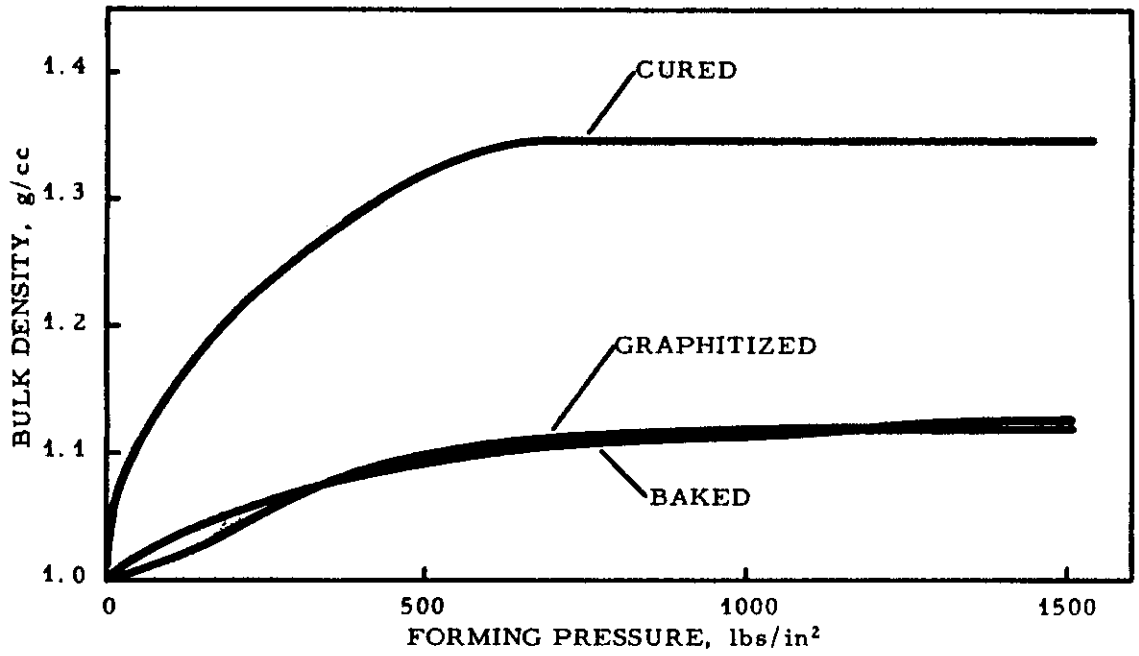

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Figure 2. Bulk Density versus Forming Pressure for Macerated-Graphite-Cloth Composites

2.1.1.2. Physical Properties of Macerated Composites from Initial Studies

The forming equipment available for scale-up in the development of fibrous composites consisted of a 29-ton press and a 9 $^3/_4$-inch diameter electrically heated mold permitting a maximum molding pressure of 750 lbs/in^2. Since this pressure was within the 600 to 1000 lbs/in^2 range previously selected, plugs for initial physical property measurements were formed at 750 lbs/in^2 with a binder level of 50 parts per hundred.

A mixture of the macerated graphite cloth (grade WCA) and resin (50 parts per hundred by weight) was prepared, charged to the mold and pressure cured for 6 hours at 130°C. The cured plug was baked to 800°C and graphitized to 2800°C with samples being taken for physical property measurement at each stage of processing.

The properties of the cured (PT-0112), *baked (PT-0113), and graphitized (PT-0114) materials made from WCA graphite cloth are shown in Table 2. The thermal conductivities of the above materials

Table 2. Properties of Macerated-Graphite-Cloth Composites

Composite Processing Temperature, °C	130	800	2800
Grade	PT-0112	PT-0113*	PT-0114*
Bulk Density, g/cc	1.26	1.06	0.96
Flexural Strength, lbs/in^2			
w.g.	2900	1400	1000
a.g.	600	450	480
Compressive Strength, lbs/in^2			
w.g.	11000	2700	1600
a.g.	9100	900	800
Young's Modulus, 10^6 lbs/in^2			
w.g.	1.28	0.67	0.94
a.g.	0.53	0.46	0.52
Specific Resistance, 10^{-4} ohm-cm			
w.g.	300	100	60
a.g.	900	400	90
Thermal Conductivity, BTU-ft/ft^2 hr° F			
w.g.	2.3	3.8	19.0
a.g.	1.4	1.8	9.4
Shrinkage, per cent			
w.g.	1.6	0.5	
a.g.	2.8	0.6	
Weight-Loss, per cent	18.3	3.3	

N = 5 for all entries except thermal conductivity where N = 2

* See appendix for description of various grades; see Table 10 for final properties of PT-0113 and PT-0114

representing various processing states are of special interest. For example, grade PT-0114 fibrous graphite, even though it has been fully graphitized, has a thermal conductivity of only 19 BTU-ft/ft^2 hr °F while grade ATJ, a fine-grain premium graphite, has a thermal conductivity of 68 BTU-ft/ft^2 hr °F.

2.1.1.3. Effect of Filler Material Type on Macerated Graphite-Cloth Composites

An experimental grade of graphite cloth, WC-0066, produced from a new raw material, was shown to have tensile strength approximately twice that of WCA cloth while other properties of the two grades were very similar as shown in Table 3. The WC-0066 cloth, because of its higher tensile strength, was evaluated as the macerated filler material in fibrous composites. WCA cloth was also included in the evaluation as a basis for comparison.

Table 3. Property* Comparison for WCA and WC-0066 Graphite Fabrics

Cloth Grade	Exper. Grade WC-0066	Grade WCA
Final Processing Temperature, °C	2800	2800
Surface Area, m^2/g	1.98	2.0
Weight, oz/yd^2	7.3	7.3
Count		
Warp	28	29
Fill	26	25
Gauge, inches	0.022	0.023
Tensile Strength, lbs		
Warp	16.6	9.0
Fill	13.3	7.7

* R. O. Moyer, unpublished data, National Carbon Company Development Laboratory, SMR August, 1960

Mixtures of each cloth and resin binder were prepared at a binder level of 50 parts per hundred by weight in a manner similar to that previously described. The mixes were formed, at a pressure of 750 lbs/in^2, into 9 $^3/_4$-inch diameter plugs, pressure cured for 6 hours at 130 - 150°C, baked to 800°C and graphitized to 2800°C.

Properties of the baked (PT-0113) and graphitized (PT-0114) materials incorporating each of the two fillers are compared in Table 4. The

Table 4. Properties of Macerated-Graphite-Cloth Composites

Type Filler	Graphite Cloth			
	WCA		WC-0066*	
Cloth Grade	Grade		Exper. Grade	
Composite Processing Temperature, °C	800	2800	800	2800
Grade	PT-0113	PT-0114	PT-0113	PT-0114
Bulk Density, g/cc	1.11	1.00	1.20	1.16
Flexural Strength, lbs/in^2				
w.g.	1700	1700	1700	1960
a.g.	300	500	500	780
Young's Modulus, 10^6 lbs/in^2				
w.g.	1.13	0.78	1.43	1.14
a.g.	0.32	0.24	0.52	0.47
Specific Resistance, 10^{-4} ohm-cm				
w.g.	100	30	80	40
a.g.	240	70	160	60

*WC-0066 - Experimental, or development grade

two fillers produced very little difference in the properties of the baked or PT-0113 form. In the graphitized state, however, the PT-0114 using WC-0066 cloth had a with-the-grain flexural strength of 1960 lbs/in^2 as compared to 1700 lbs/in^2 for the WCA filler while the across-the-grain flexural strengths were 780 and 500 lbs/in^2, respectively. The PT-0114 composite fabricated from WCA also showed a strength improvement over data previously cited in Table 2. Refinement of the process by which the WCA graphite cloth was produced had gradually improved the tensile strength of the cloth; therefore, the flexural strength increase of the composites in this experiment was attributed to the improved tensile strength of both WCA and WC-0066 grades. This conclusion did not take into account the difference in fiber lengths caused by shredding or macerating time. The dependency of composite strength on this variable will be explained in Section 2.1.2.2.

2.1.1.4. Effect of the Oxidation of Graphite Cloth on Composite Strength

In one method of oxidation, strips of cloth were placed on copper-

mesh screens in the stagnant air of a muffle furnace (preheated to 600°C) and oxidized for 15 minutes. The oxidized cloth was mixed with resin at 50 parts per hundred by weight and shredded into a fibrous mixture. The mixture was then formed into a 5-inch diameter plug at a pressure of 750 lbs/in^2 and cured to approximately 150°C. The strength of the cured composite was significantly improved by controlled oxidation of the filler. The properties of plugs fabricated from oxidized and from unoxidized cloth are shown in Table 5.

Table 5. Effect of Controlled Oxidation on Strength of Cured (PT-0112) Macerated Composites

	Unoxidized Control	Oxidized
Flexural Strength, lbs/in^2		
w. g.	1900	2700
Compressive Strength, lbs/in^2		
w. g.	2800	6200
a. g.	7300	9200

Another method for oxidizing the graphite cloth used carbon dioxide generated from the decomposition of calcium carbonate. The chemical reactions are illustrated by the following formulae:

(1) Decomposition of calcium carbonate

$$CaCo_3 \xrightarrow{+825°C} Cao + CO_2$$

(2) Oxidation of graphite cloth by carbon dioxide

$$CO_2 + 2C \xrightarrow{+825°C*} C + 2CO$$

* Set by $CaCO_3$ Decomposition Temperature

Calcined petroleum coke sized to pass through a 1 $^1/_2$ mesh screen and be retained on a 3 mesh screen was blended with ten per cent by weight of powdered limestone to form a coke-limestone packing material. Single layers of the graphite cloth were separated by $^1/_2$ inch of the coke-limestone pack in a ceramic sagger. The sagger was sealed with silica sand, heated to 900°C and held for 24 hours. Plugs were fabricated from the oxidized and from the unoxidized-control graphite by the method previously described. Properties were measured on the two plugs after baking

and graphitizing and the results are shown in Table 6.

Table 6. Effect of Controlled Oxidation on Properties of Macerated (PT-0114) Composites

	Oxidized	Unoxidized Control
Bulk Density, g/cc	1.26	1.05
Young's Modulus, 10^6 lbs/in^2	1.04	0.60
Flexural Strength, lbs/in^2	1900	840

2.1.2. Advanced Studies, Macerated-Graphite-Cloth Composites

Availability of additional forming equipment allowed re-evaluation of the various parameters associated with macerated-graphite-cloth composites. Definitive tests rather than abbreviated methods were used to establish the optimum forming pressure and binder level for these composites. In some cases, changing the parameters necessitated re-characterization of the macerated composites.

2.1.2.1. Re-evaluation of Binder Level and Forming Pressure from Advanced Studies

A re-evaluation of the optimum binder level was conducted on macerated composites made from WCA graphite cloth because the initial selection of binder level and forming pressure had been based on plugs too small for comprehensive property measurements. The binder level was evaluated by blending macerated graphite cloth and the furane-phenolic resin system prepared in mixtures ranging from 40 to 70 parts of binder per hundred parts by weight of filler. Weighed quantities of these mixtures were charged to an electrically heated mold and fabricated into plugs 5 inches in diameter by 5 inches in length. The plugs were cured at 130°C under pressures of 770, 1025 and 1535 lbs/in^2, baked to 800°C and graphitized to 2800°C. Flexural strengths and bulk densities were measured on $^1/_2$-inch cross section by 4-inch length samples cut from the with-grain and across-grain direction of the graphitized plugs and the results of these measurements are recorded in Table 7.

Table 7. Bulk Densities and Flexural Strengths of Graphitized-(PT-0114) Macerated-Graphite-Cloth* Composites at Various Binder Levels and Forming Pressures

Forming Pressure Gauge lbs/in²	Product lbs/in²	Binder Level PPH	Binder Level Weight Per Cent	Bulk Density g/cc	Flexural Strength lbs/in² W. G.	Flexural Strength lbs/in² A. G.
300	770	40	28.6	0.93	1480	260
300	770	50	33.3	1.23	1590	260
300	770	55	35.5	1.08	1120	230
300	770	60	37.5	1.11	1100	240
300	770	70	41.3	1.10	900	200
400	1025	40	28.6	1.01	1700	320
400	1025	50	33.3	1.26	1800	340
400	1025	55	35.5	1.14	1100	190
400	1025	60	37.5	1.11	1000	230
400	1025	70	41.3	1.10	960	350
600	1535	40	28.6	1.10	1730	450
600	1535	50	33.3	1.23	2040	570
600	1535	55	35.5	1.11	1650	500
600	1535	60	37.5	1.14	1750	470
600	1535	70	41.3	1.10	1580	360

* WCA Graphite Cloth

The with-grain flexural strengths, plotted as a function of binder level in Figure 3, show the optimum binder level to be approximately 50 parts per hundred, regardless of forming pressure. Binder levels above 50 parts per hundred result in excess resin being entrapped in the formed article during curing. This excess of resin lowers the composite flexural strength by introducing stresses or microflaws.

The problem related to binder level is the uniform distribution of the resin to the fibers. As previously discussed, the resin distribution is accomplished by randomly pouring the resin onto the graphite cloth before charging the cloth to the mixer. As the cloth is shredded

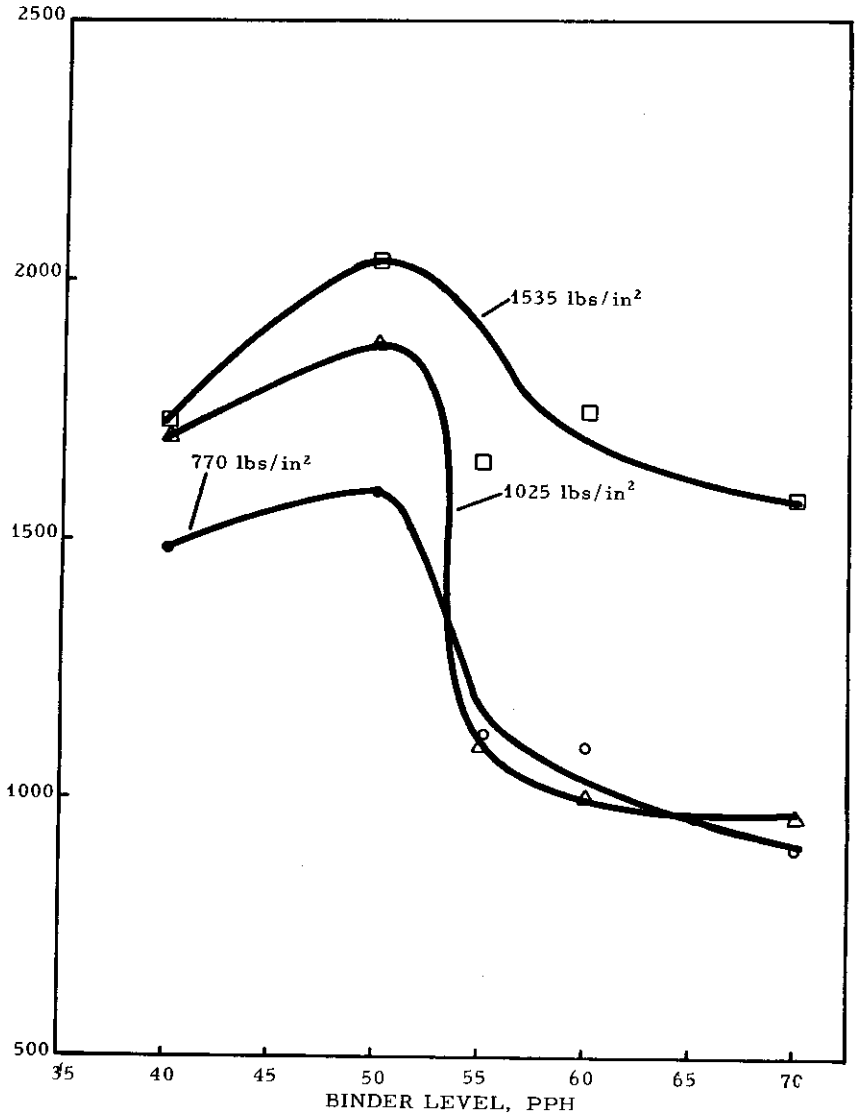

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Figure 3. With-the-Grain Flexural Strength of PT-0114 versus Binder Level at Various Forming Pressures, Graphitized- (PT-0114) Macerated-Graphite-Cloth Composites

or macerated by the mixer blades, the resin is distributed to the fibers. Although the final mixture assumes a moist, fluffy nature without apparent binder agglomerates, this method obviously does not provide the ultimate in binder distribution.

Saturating the graphite cloth with resin and passing it through a squeeze-roll was investigated as a technique for obtaining uniform distribution of the resin. Strips of WCA graphite cloth were saturated in a vat of the resin preheated to 55 - 60°C. The cloth was passed through a primary distributor, consisting of two pieces of strap metal separated approximately 0.040 inch, to remove part of the excess resin. Final resin treatment consisted of passing the cloth strips between two stainless steel squeeze-rolls 0.012 inch apart. Resin content of the cloth after this operation was approximately 110 parts per hundred and repeated passes through the squeeze-rolls did not reduce it appreciably. The spacing between the squeeze-rolls was decreased, but the increased pressure was detrimental to the cloth. Although the binder level was above the selected optimum of 50 parts per hundred, the resin treated cloth was macerated in the bread mixer and formed into a 5-inch diameter plug and cured for 4 hours at 125°C under a pressure of 770 lbs/in^2. Extrusion of small quantities of the mix around the mold punches during curing was apparently caused by excess resin. The plug was packed in coke, baked to 800°C and graphitized to 2800°C in a nonoxidizing atmosphere. Examination after graphitization revealed small hairline cracks typical of excess binder. It was concluded that this technique could not be used for applying and distributing the resin to graphite cloth for macerated composites because indications were that the binder level could not be reduced to the optimum of 50 parts per hundred.

After establishing the binder level at 50 parts per hundred, an investigation was made to determine the optimum forming pressure for macerated composites. A mixture of WCA graphite cloth and resin (50 parts per hundred) was prepared and used to fabricate 5-inch diameter plugs at various pressures ranging from 510 to 2050 lbs/in^2. These plugs were cured under pressure for 4 hours at 125°C, baked to 800°C, and subsequently graphitized to 2800°C. Graphitized properties of these plugs are shown in Table 8. The optimum forming pressure, as indicated by the flexural strength of the graphitized composites reported in Table 8, was approximately 1535 lbs/in^2 instead of the previously selected 750 lbs/in^2. (See Figure 3)

Table 8. Effect of Forming Pressure on Properties of Macerated-Graphite-Cloth* Composites (PT-0114)

Forming Pressure Gauge lbs/in²	Forming Pressure Product lbs/in²	Bulk Density g/cc	Young's Modulus 10^6 lbs/in² W.G.	Young's Modulus 10^6 lbs/in² A.G.	Specific Resistance 10^{-4} ohm-cm W.G.	Specific Resistance 10^{-4} ohm-cm A.G.	Flexural Strength lbs/in² W.G.	Flexural Strength lbs/in² A.G.
200	510	1.01	0.68	----	46.0	120.0	970	130
250	640	1.05	0.85	0.32	40.5	70.0	1400	520
300	770	1.05	0.86	0.33	38.0	67.0	1500	640
350	900	1.08	0.95	0.34	36.0	65.0	1830	610
400	1025	1.07	1.03	0.39	32.0	56.0	1880	780
500	1280	1.20	1.08	0.44	37.0	73.0	2000	600
600	1535	1.20	1.22	0.49	34.0	57.9	2400	700
700	1790	1.11	1.14	0.47	33.6	56.7	2200	670
800	2050	1.10	1.22	0.52	39.9	64.4	2150	740

* WCA Graphite Cloth

N = 5 for all entries except bulk density where N = 10

2.1.2.2. Effect of Shredding Time on Properties of Macerated-Graphite-Cloth Composites

Unexplained strength variations were experienced in fibrous composites formed from WC-0066 and WCA graphite cloth. All previous work on macerated-graphite-cloth had disregarded the effect of shredding time on the strength of the composites. The shredding period had been dictated by the time required to reduce the graphite cloth and resin to a fibrous mix with no consideration being given to reducing the fiber lengths further by additional shredding.

A limited study of the effect of shredding time was made with WC-0066 and WCA graphite cloths. Filler-resin mixtures with each of these two cloths were prepared at a binder level of 50 parts per

hundred. To avoid any possibility of variation from mix to mix, a suitable quantity of the cloth-resin mixture was made and samples were withdrawn from the mixer after 30, 40, 50, 60 and 120 minutes of shredding. Samples of WCA and WC-0066 mixes compared after each of the shredding intervals showed a considerable difference in degree of "shreddability" even for the short times. For example, the WCA graphite cloth was reduced to the usual consistency in approximately 60 minutes but the stronger WC-0066 required 120 minutes of shredding to obtain a comparable mix.

Each of the cloth-resin mixtures was formed at 1535 lbs/in^2 into a 5-inch diameter plug which was cured for 3 hours at 125°C. Property measurements, made on samples cut from the plugs after baking and graphitizing, are shown in Table 9. A plot of flexural

Table 9. Effect of Shredding Time on Properties* of Macerated-Graphite-Cloth Composites (PT-0114)

	WCA Graphite-Cloth Filler				WC-0066 Graphite Cloth Filler			
Shredding Time Minutes	Bulk Density g/cc	Young's Modulus 10^6 lbs/in^2	Specific Resistance 10^{-4} ohm-cm	Flexural Strength lbs/in^2	Bulk Density g/cc	Young's Modulus 10^6 lbs/in^2	Specific Resistance ohm-cm by 10^{-4}	Flexural Strength lbs/in^2
30	1.24	1.02	35.7	1760	1.08	0.76	33.4	1580
40	1.24	1.12	34.7	1840	1.06	0.82	33.4	1610
50	1.25	1.16	34.2	1920	1.06	0.81	34.5	1560
60	1.26	1.19	34.9	2220	1.07	0.88	33.9	1570
120	1.29	1.25	34.2	2200	1.07	0.82	35.8	1540

* All properties measured with the grain

N = 5 for all entries

strength versus shredding time for WCA and for WC-0066 graphite cloth is shown in Figure 4. The flexural strength of WCA composites was enhanced by the longer shredding time with strength increases of approximately 500 lbs/in^2 being obtained by increasing the shredding time from 30 to 60 minutes. Evidently, the optimum shredding time was between 60 and 120 minutes. The longer shredding time seemed to give a more aggregate mixture which, when formed into a plug, gave much better bonding and a more uniform product. The increased shredding time with WC-0066 cloth slightly, but not significantly, decreased the composite strength. Although the appearance of the mix was noticeably different, a decrease in flexural strength of only 40 lbs/in^2 was obtained by shredding for 120 minutes rather than 30 minutes.

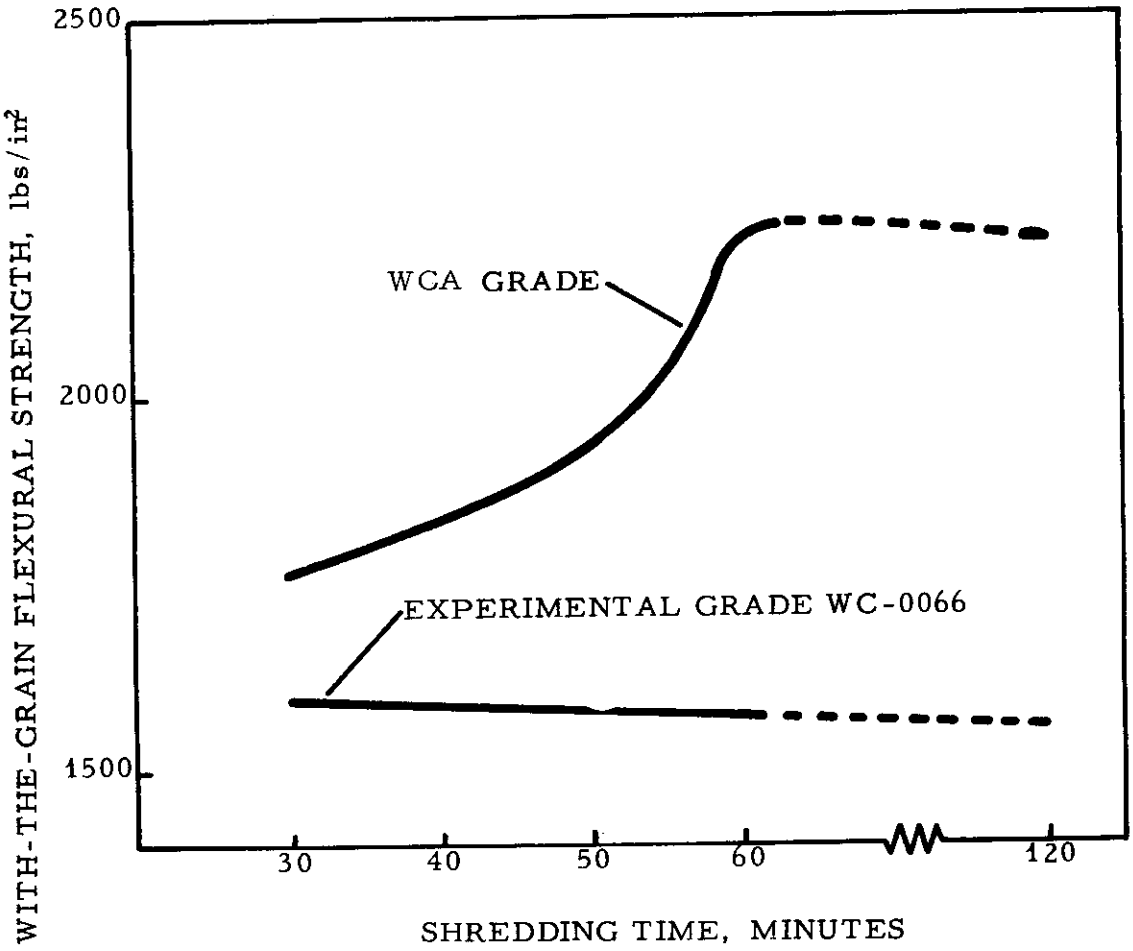


Figure 4. Flexural Strength versus Shredding Time for PT-0114 Composites of WCA and WC-0066

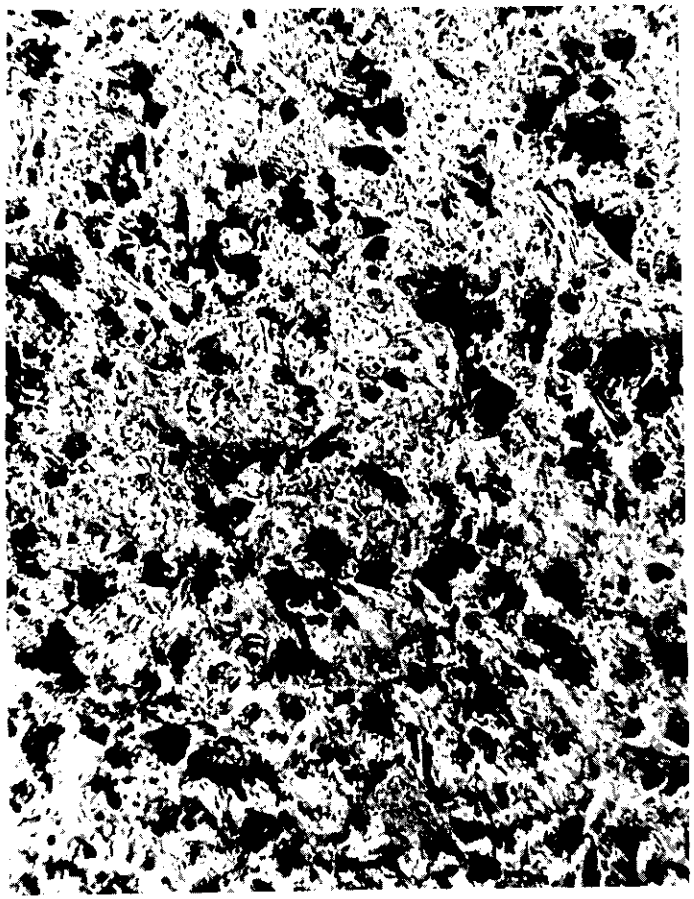
2.1.2.3. Characterization of Macerated-Graphite-Cloth Composites

Samples for characterization of these fibrous macerated composites were prepared from WCA graphite-cloth filler material using a binder level of 50 parts per hundred and a forming pressure of 1535 lbs/in^2. Properties measured on both the baked (PT-0113) and graphitized (PT-0114) are shown in Table 10 with the properties of grade ATJ graphite as a comparison. Especially interesting among these properties are the specific strength (strength in lbs/in^2 divided by bulk density in lbs/in^3), bulk density and thermal conductivity. For example, grade ATJ, a fine-grain premium grade of graphite, has a specific strength of 64,000 inches, a bulk density of 1.73 g/cc, and a thermal conductivity of 68 BTU-ft/hr°F ft^2. Grade PT-0114 fibrous graphite has a nearly comparable specific strength (56,000 inches) at a much lower bulk density (1.19 g/cc), and one-fifth the thermal conductivity (12.2 BTU-ft/hr°F ft^2) of grade ATJ. A threefold reduction in thermal conductivity is offered by the PT-0113 carbon composite but with a 20 per cent sacrifice in strength. The fibrous microstructure of grade PT-0114 as compared to the structure of grade ATJ is shown in Figure 5.

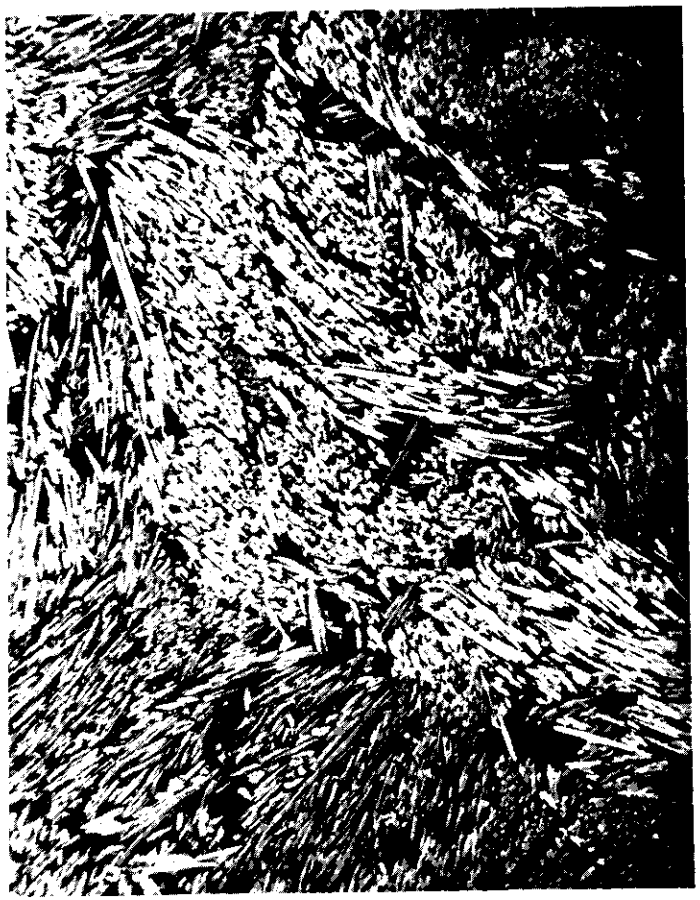
Table 10. Typical Room Temperature Physical Properties of Macerated-Graphite-Cloth Composites and Grade ATJ Graphite

Grade	PT-0113			PT-0114			ATJ	
Processing Temperature, °C	800			2800			2800	
	Number Samples	Ave.	σ	Number Samples	Ave.	σ	Ave.	σ
Bulk Density, g/cc	44	1.18	0.04	67	1.15	0.02	1.73	0.04
Specific Resistance 10^{-4} ohm-cm								
w.g.	32	119.8	15.0	35	31.0	1.99	11.0	1.68
a.g.	17	288.6	45.8	32	62.0	4.66	14.5	1.45
Flexural Strength, lbs/in^2								
w.g.	14	2060	227	12	2450	341	4010	773
a.g.	8	440	62	13	730	80	3580	484
Compressive Strength, lbs/in^2								
w.g.	6	2970	339	6	2040	376	8270	1028
a.g.	6	3700	349	6	2520	245	8540	1144
Young's Modulus, 10^6 lbs/in^2								
w.g.	29	1.23	0.13	35	0.89	0.07	1.45	0.17
a.g.	15	0.43	0.06	32	0.28	0.03	1.15	0.09
CTE (25-100°C), 10^{-6}/°C, w.g.	3	1.32	--	3	1.00	--	2.3	0.22
Thermal Conductivity, BTU-ft/hr °F ft^2								
w.g.*	2	3.2	--	2	12.2	--	65.1	--
a.g.	2	1.7	--	2	6.6	--	52.2	--
Specific Strength, inches*		38,820			59,180		64,000	

* Flexural Strength in lbs/in^2 divided by bulk density in lbs/in^3



Grade ATJ



Grade PT-0114

Figure 5. Photomicrographs of Grades PT-0114 and ATJ Graphite (100X) Demonstrating Fibrous Nature of Composite Material

Many high temperature applications anticipated for fibrous composites require a completely temperature-stabilized article and, because of its higher processing temperature, grade PT-0114 is more suitable for these applications than is grade PT-0113. Both of these grades are easily machined with standard equipment. Machinability is difficult to define numerically but it is illustrated graphically in Figure 6 which shows two views of test cones machined from grade PT-0114. The sharpness of the thread crests and roots illustrates the ability of this material to be machined to feathered edges without chipping.

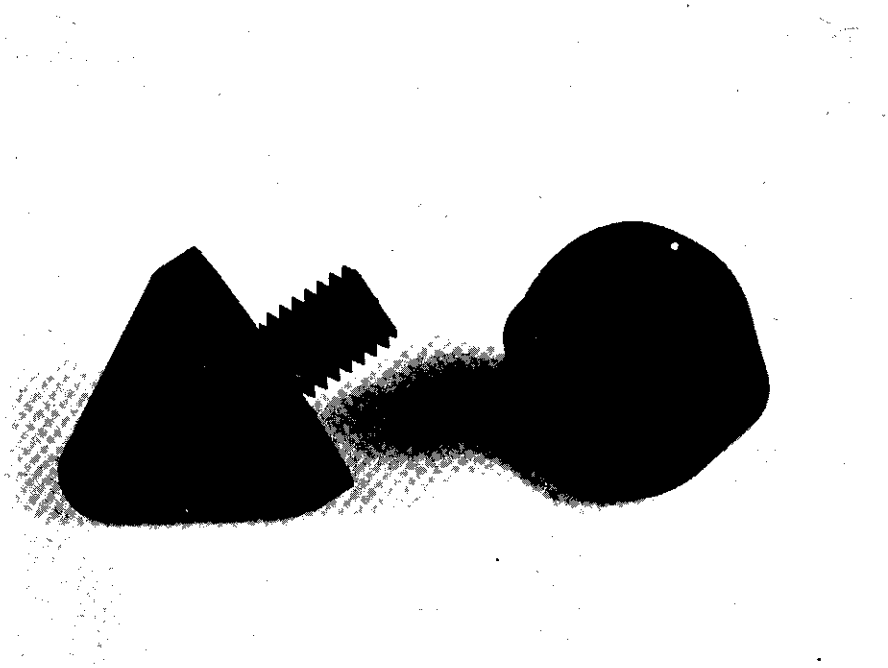


Figure 6. Test Cones Demonstrating Machinability of Grade PT-0114 Graphite

The flexural strength of grade PT-0114 has been measured from room temperature to 2500°C and the results are shown in Figure 7.

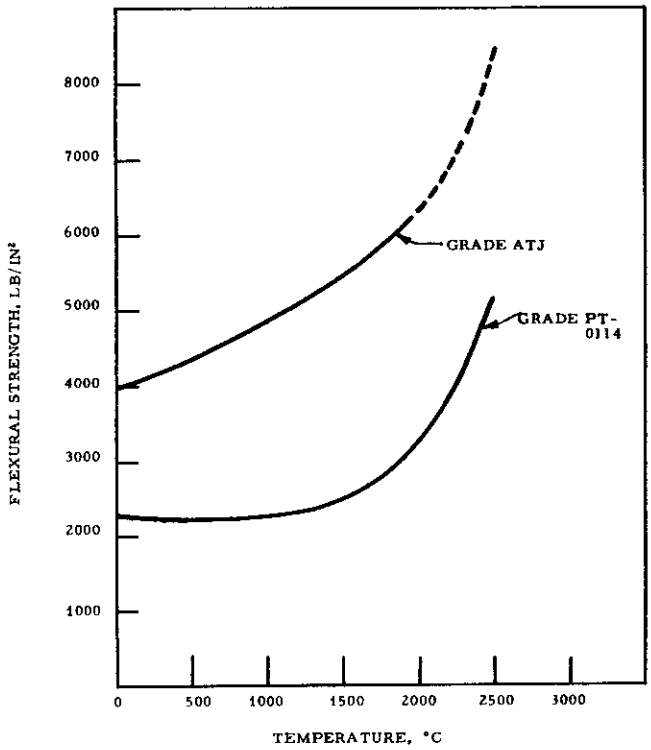


Figure 7. Flexural Strength Comparison of Grades PT-0114 and ATJ Graphite at Elevated Temperatures

Following the behavior of other graphites, such as grade ATJ, the strength increased markedly between 2000°C and 2500°C. An attempt to measure flexural strength at 2750°C resulted in marked plastic deformation as shown in Figure 8.

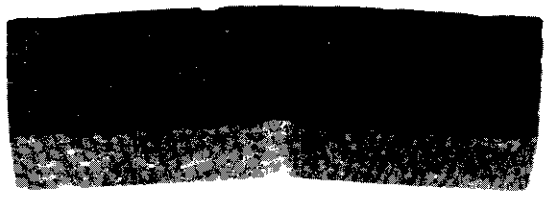


Figure 8. Flexural Strength Specimen of Grade PT-0114 Demonstrating Plastic Deformation at 2750°C

2.2. Graphite-Cloth Laminates

Graphite-cloth laminates were fabricated from multi-layers of resin-impregnated cloth. Impregnation was accomplished by saturating single layers of cloth with resin and passing it through stainless steel squeeze-rolls separated a predetermined distance. After being cut into swatches, the cloth was stacked into multi-layers and formed into a laminate by pressure curing between the heated platens of a press. The cured laminate was then baked and graphitized to yield a thermally stable material.

The availability of new grades of graphite cloth has facilitated the evaluation of factors related to the filler material which influence the laminate properties. These factors are tensile strength and weave structure of the graphite cloth each of which was considered in selecting a filler material which would produce a structurally-sound, thermally-stable, graphite-cloth laminate. After the filler material was selected, the effect of precuring and utilizing a pitch binder on the laminate properties was evaluated.

2.2.1. Effect of Graphite Cloth Strength on the Flexural Strength of Laminates

WCA and WC-0066 graphite cloth were used to determine the effect of graphite cloth strength on laminate strength since the tensile strength (Table 3) of WCA is 9.0 by 7.7 lbs/inch in the warp and fill directions, respectively, as compared to 16.3 by 13.3 lbs/inch for WC-0066. Other than in strength, these materials do not seem to differ significantly.

The graphite cloth (WCA or WC-0066) was resin-treated in 5-inch wide strips, passed through stainless steel squeeze-rolls 0.015 inch apart, and cut into 5-inch square swatches. Forty-five of these swatches were stacked one on top of the other, and placed between the platens of a hydraulic press as shown in Figure 9. The mechanical pressure was applied and the platens were heated electrically to cure the laminate. Five laminates were fabricated by this technique from each WCA and WC-0066 graphite cloth. To determine the optimum forming pressure, laminates were formed at pressures ranging from 50 to 250 lbs/in^2 for the WC-0066 and WCA grades, respectively. Since pressure and binder level are interdependent for laminates, determination of the optimum forming pressure will result in the optimum binder level. After the laminates were baked and graphitized, samples were taken for property determinations. The cured resin content (weight per cent) of the laminate and the graphitized bulk density and flexural strength were

measured on five samples from each laminate. The averages of these five measurements for WCA and WC-0066 are listed in Table 11.

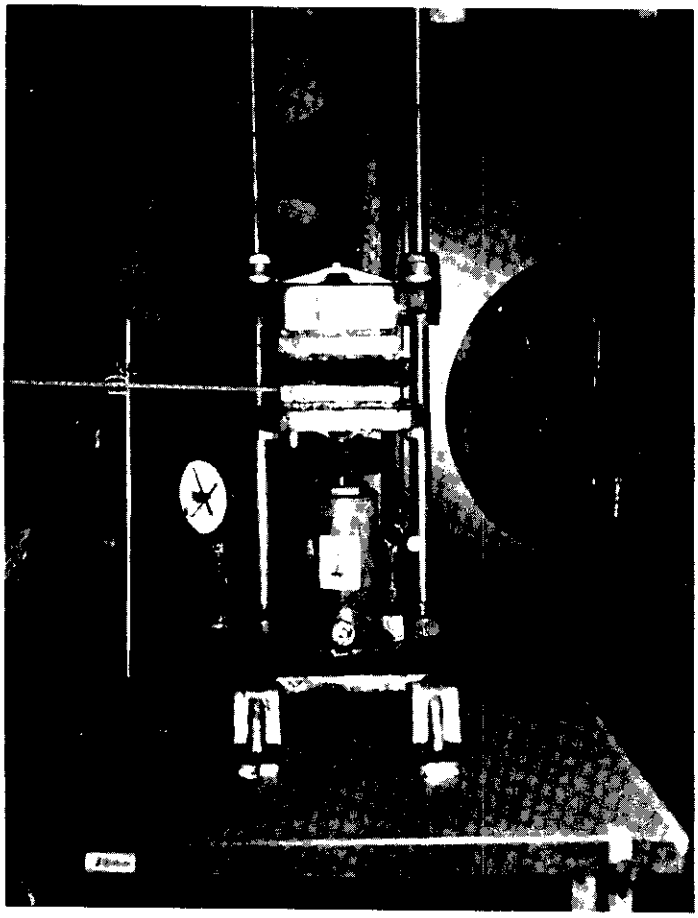


Figure 9. Press Employed for the Fabrication of Laminated-Graphite-Cloth Test Specimen

Table 11. Effect of Forming Pressure on the Properties* of WC-0066 and WCA Graphite-Cloth Laminates

	WC-0066 Graphite-Cloth Laminates					WCA Graphite-Cloth Laminates				
Forming Pressure, lbs/in^2	50	100	150	200	250	50	100	150	200	300
Resin Content, weight per cent	32.8	29.5	26.7	24.8	24.6	37.2	32.8	29.4	27.3	26.4
Bulk Density, g/cc	1.05	1.08	1.10	1.11	1.12	1.08	1.11	1.17	1.17	1.20
Flexural Strength, lbs/in^2	1630	1790	1930	2050	1750	2250	2560	3200	2330	1770

* All properties measured with the grain

The resin content of the laminates in the two series is plotted as a function of forming pressure in Figure 10. The decrease in resin content was due to flow from the laminate under the influence of the forming pressure. The initial resin content of the WC-0066 cloth was 7.5 per cent higher than that of WCA cloth but the retention of resin for WCA was between 2.5 and 4.4 per cent higher at all forming pressures which probably accounted for the consistently higher strengths of the WCA laminates.

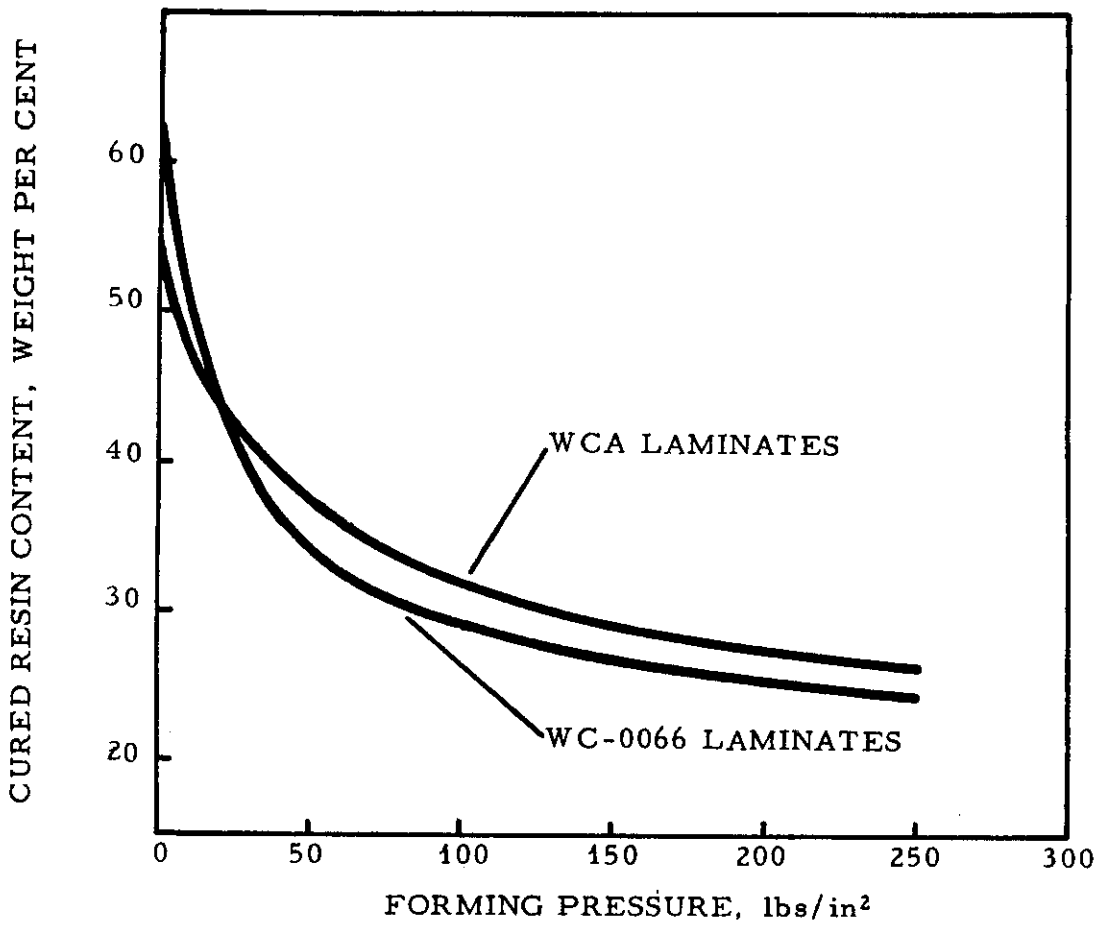


Figure 10. Effect of Forming Pressure on Resin Content of Graphite-Cloth Laminates

A plot of flexural strength versus forming pressure for the two series is shown in Figure 11. The flexural strength of the WCA laminates reached a maximum of 3200 lbs/in^2 at a forming pressure of 150 lbs/in^2. WC-0066 cloth laminates had a peak flexural strength of 2050 lbs/in^2 at a forming pressure of 200 lbs/in^2. The laminate strength was expected to increase with improved filler strength, but the converse was found to be true. This decline in flexural strength

was attributed to the ability of the WCA cloth to retain a larger quantity of resin which, when pyrolyzed, increased the amount of resin coke.

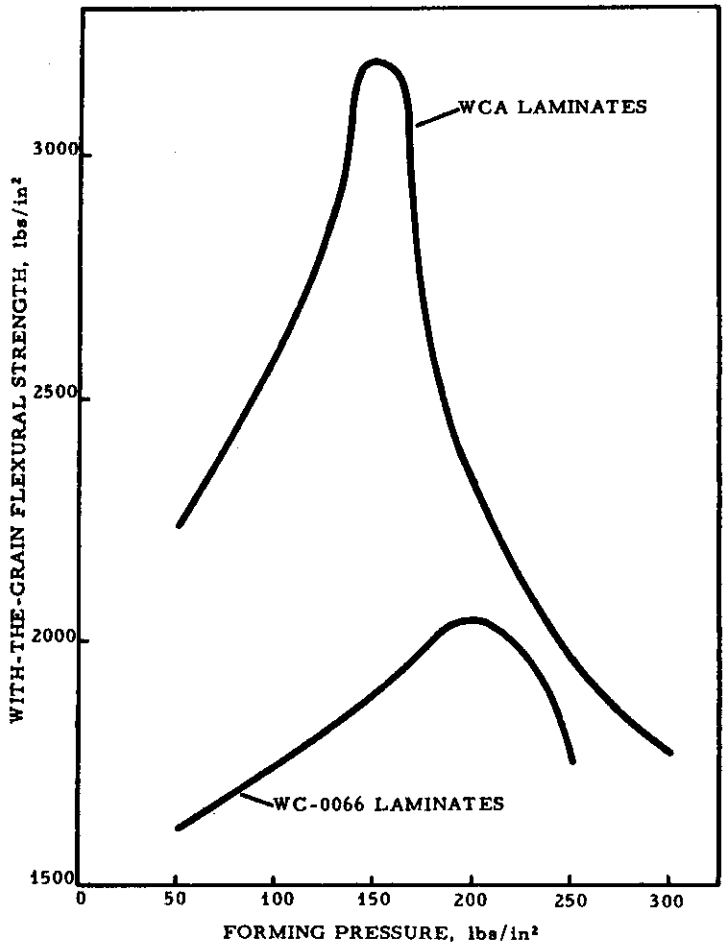


Figure 11. Flexural Strength versus Forming Pressure for PT-0111 Cloth Laminates

2.2.2. Effect of Weave Structure on the Flexural Strength of Graphite-Cloth Laminates

Thermally-stable laminates for evaluating the effect of weave structure on flexural strength were fabricated from WCH graphite cloth and compared to laminates produced from WCA graphite cloth. WCH is a standard twill weave fabric while WCA is a standard square weave. The laminates were formed, processed, and measured for properties according to the methods described in Section 2.2.1. The properties of these WCH laminates are shown in Table 12 and the cured resin content as a function of forming pressure is shown graphically in Figure 12.

Table 12. Effect of Forming Pressure on Properties of WCH Graphite-Cloth Laminates

Forming Pressure, lbs/in^2	25	50	100	150	200
Resin Content, Weight per cent	34.5	33.1	29.3	28.0	24.6
Bulk Density, g/cc	1.06	1.08	1.12	1.12	1.12
Specific Resistance, 10^{-4} ohm-cm	22.43	20.90	21.80	21.47	25.02
Flexural Strength, lbs/in^2	1580	1730	2120	2280	2000

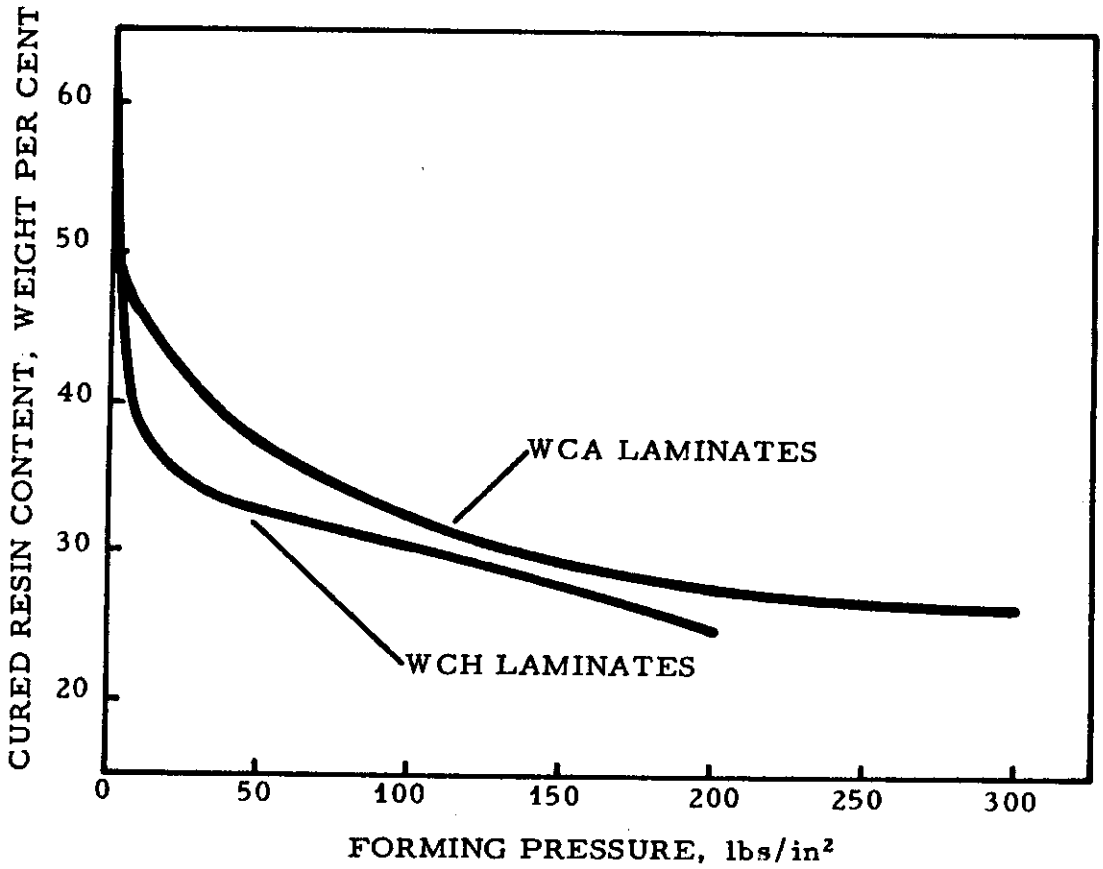


Figure 12. Effect of Forming Pressure on Cured Resin Content of WCH and WCA Laminates

Also shown in Figure 12 is the resin content of the WCA laminate series previously described. Although the WCH material absorbed more resin initially, the WCA material retained a greater quantity of the resin. Flexural strengths of graphitized laminates made from WCH and WCA cloths, plotted as a function of forming pressure in Figure 13, showed that the flexural strength of WCH cloth laminates was much lower than that for WCA cloth. The peak flexural strength of WCH laminates was 2280 lbs/in^2 at a forming pressure of 150 lbs/in^2 while WCA graphite-cloth laminates had a peak flexural strength of 3200 lbs/in^2 at the same forming pressure.

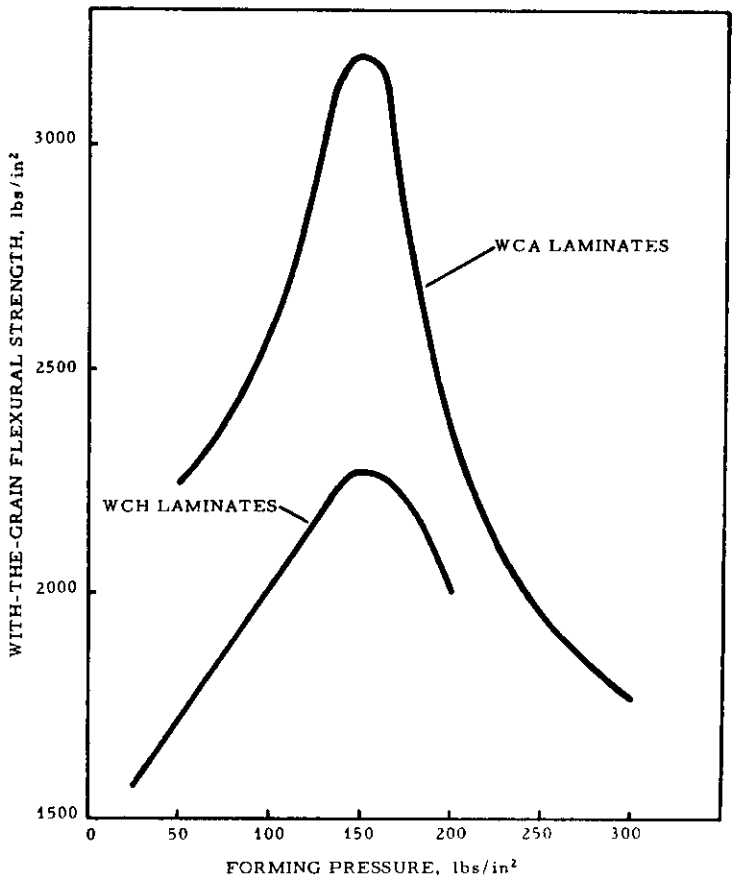


Figure 13. Flexural Strength Comparison for Graphitized WCH and WCA Cloth Laminates

These findings showed that WCA graphite cloth produced much stronger thermally-stable laminates than either the WC-0066 (Section 2.2.1) or WCH filler. WCA cloth, therefore, was used in all additional laminate studies.

2.2.3. Property Characterization of WCA Graphite-Cloth Laminates

After it was definitely established that WCA graphite cloth is a superior filler for cloth laminates, additional physical property data were obtained on these structures. Laminates for additional property measurements and characterization were fabricated from WCA graphite cloth at a pressure of 150 lbs/in^2 and processed according to the method described in Section 2.2.1. Although only the graphitized properties (grade PT-0111) were considered in selecting the optimum forming pressure, the properties of the baked laminate (grade PT-0110) formed under the same conditions were also measured. A summary of the data is shown in Table 13.

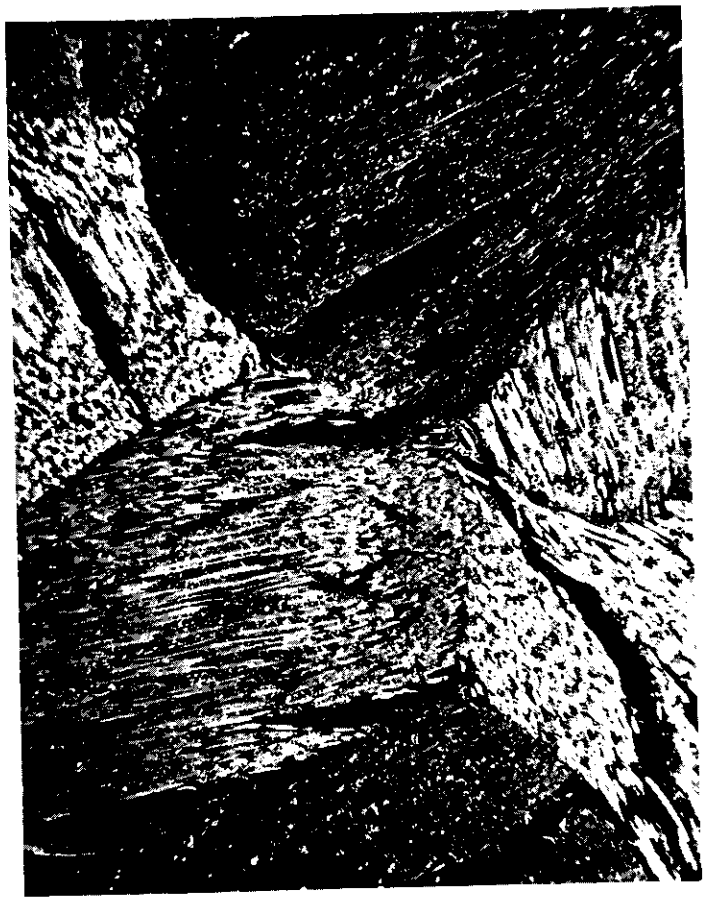
Table 13. Typical Room Temperature Properties of Laminated-Graphite-Cloth Structures

Grade		PT-0110	PT-0111
Processing Temperature, °C		800	2800
Bulk Density, g/cc		1.20	1.16
Specific Resistance, 10^{-4} ohm-cm	w.g.*	105.5	25.0
Flexural Strength, lbs/in^2	w.g.	2200	3200
Young's Modulus, 10^6 lbs/in^2	w.g.	0.84	1.05
Compressive Strength, lbs/in^2	w.g.	2500	1175
	a.g.	6400	9080
Tensile Strength, lbs/in^2	w.g.	2000	2700
Specific Strength, ** inches	w.g.	51000	76500

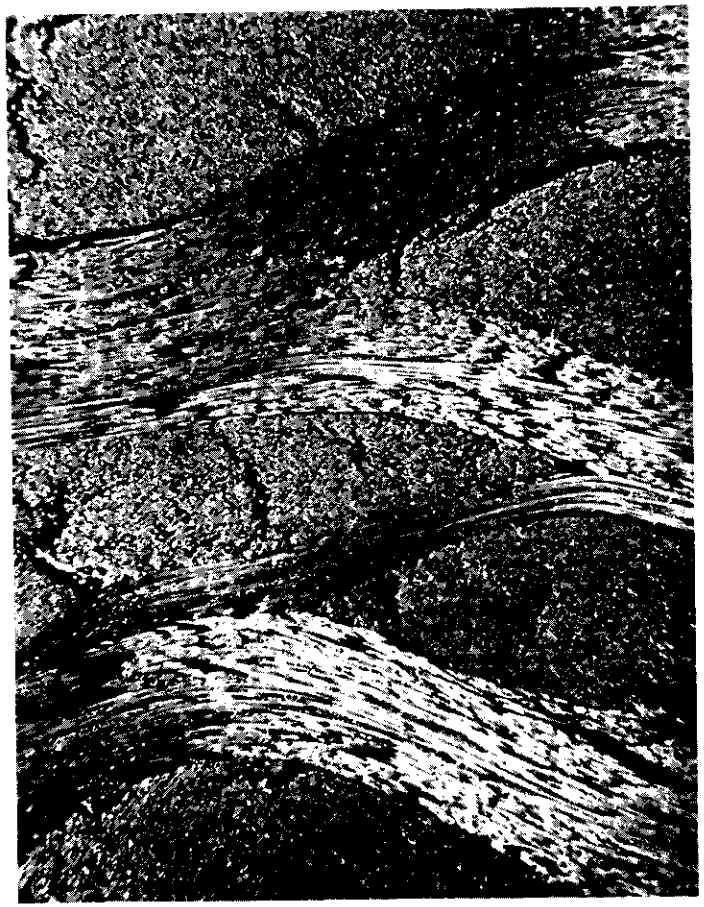
* With the grain, a.g. Across the grain
** Based on flexural strength in lbs/in^2 and bulk density in lbs/in^3

N = 5 for all entries

The PT-0111 grade laminates had with-the-grain flexural strengths 25 per cent, or 800 lbs/in^2, greater than those of the macerated composites utilizing graphite cloth-filler. Although the orientation in the laminates improved with-the-grain strength markedly, it undoubtedly reduced the across-the-grain strength but the latter values have not been obtained because of difficulty in processing laminates of sufficient thickness to provide across-the-grain samples of a suitable size. In Figure 14, showing photomicrographs of grade PT-0111 taken with the



With the Grain



Across the Grain

Figure 14. Photomicrograph of Grade PT-0111 Graphite With and Across the Grain (100X)

grain and across the grain, the orientation of the fibers is clearly evident.

In discussing the strength of fibrous composites, it is interesting to consider the nature of the fracture obtained from flexural strength samples. Figure 15 shows broken specimens of grade ATJ, macerated (PT-0114), and laminated (PT-0111) composites. The fracture in ATJ was of a brittle nature; in the macerated composites (PT-0114) in which fibers were more or less randomly oriented, the fracture was jagged; in the PT-0111 laminate in which the fibers had one predominant direction, the fracture had a "green twig" appearance. The nature of the fracture illustrates the role played by the arrangement of the fibers.

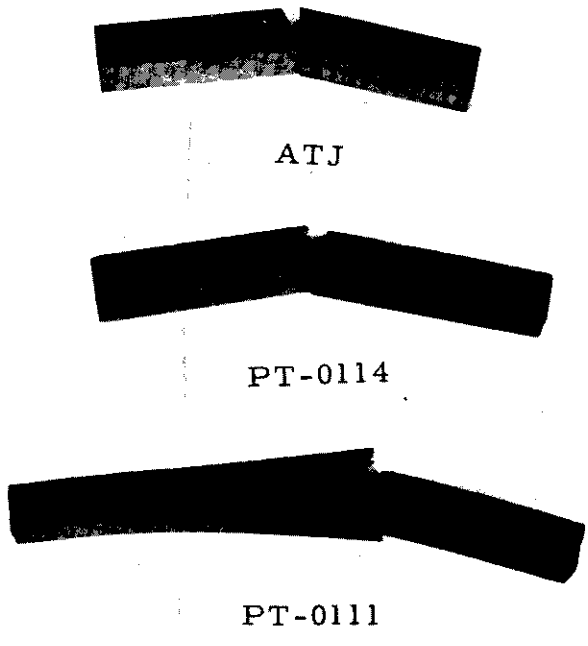


Figure 15. Comparison of Fractures Occurring in Graphite Grades ATJ, PT-0114, and PT-0111

2.2.4. Precuring Graphite Cloth for Laminate Strength Improvement

Earlier studies on graphite-cloth laminates indicated that a small increase in resin content greatly improved the laminate strength. Addition of more resin to the cloth prior to stacking in layers will not necessarily result in higher resin content in the laminate because the laminate resin content is dependent on the forming pressure, which must be high enough to place the fibers in intimate contact, and the excess resin is squeezed out at this point. The possibility of precuring the resin-coated cloth before pressure molding was investigated in an effort to increase the resin content and improve the laminate strength.

WCA graphite cloth, resin-treated as previously described in Section 2.2.1, was used in this study. The 5-inch square swatches of resin-treated cloth were placed in single layers on wire-mesh trays in an air-circulating drying oven preset at a temperature of 100°C ± 5°C. After being precured, the cloth swatches were removed from the oven, stacked in layers, and formed into a laminate at a pressure of 150 lbs/in^2. Five laminates were fabricated from cloth precured for various periods ranging from 1 to 5 minutes. The formed laminates were baked to 800°C and graphitized to 2800°C. The resin content after curing, and the bulk density and flexural strength after graphitizing were measured on five samples from each laminate. The results of these studies are given in Table 14.

Table 14. Effect of Precuring on Flexural Strength of Graphite-Cloth Laminates

Precure Time Min.	Cured Resin Content Weight Per Cent	Bulk Density g/cc	Flexural Strength lbs/in^2
5	39.3	1.15	1950
4	40.0	1.15	1970
3	35.8	1.14	1920
2	36.3	1.13	1830
1	36.0	1.12	1750
0	29.4	1.17	3200

N = 5 for all entries

These results show that precuring did result in a 7 to 10 per cent higher resin content but the laminate flexural strength is much lower than that obtained with conventionally processed laminates. The precuring operation appeared to partially polymerize the resin and decreased its bonding effectiveness.

2.2.5. Binder System Studies for Graphite-Cloth Laminates

All of the studies reported in previous sections had used the furane-phenolic resin system for the development of graphite-cloth structures. In search for new binder systems to improve further the properties and the processability of macerated cloth composites and cloth laminates, catalyzed furfural and furfuryl alcohol (1:1 by weight) and five variations of this system were investigated. The five variations of this system were prepared by adding 130°C-melting point pitch to the furfural-furfuryl alcohol in 5 per cent increments up to a maximum of 25 per cent by weight. Diethyl sulphate (4 per cent by weight) was added as a catalyst.

Strips of WCA graphite cloth 6 inches wide were dipped in the resin and passed through the stainless steel squeeze-rolls spaced 0.015 inch apart. Swatches of the resin-treated cloth 5 inches square were formed into 45-ply laminates. Five laminates with each type binder were formed at pressures ranging from 50 to 250 lbs/in^2 at intervals of 50 lbs/in^2, and cured under pressure for one hour at 125°C. The cured laminates were baked to 800°C, graphitized to 2800°C and measured for physical properties (see Table 15). Although the flexural strengths were slightly lower than those obtained with the WCA cloth and furane-phenolic resin, higher strengths are expected to result with increased additions of pitch. The pitch did not seem to be effective in improving the flexural strength until 15 per cent had been added to the furfural-furfuryl alcohol system. Above this amount of pitch, properties improved with increased forming pressure. Although an optimum forming pressure of 250 lbs/in^2 was indicated, additional trials will be necessary to establish definitely this pressure.

Several interesting observations were made during this study and additional work with this type of binder seems warranted. First, the graphite cloth appeared to have a greater affinity for the furfural-furfuryl alcohol-pitch binder than for the phenolic resin system. Although the degree of wettability probably decreases with increased additions of pitch, the system containing furfural-furfuryl alcohol and 25 per cent pitch saturates the cloth with no difficulty. Second, the laminates with the new binder cured in one-third the time usually required for the

Table 15. Properties of Pitch-Bonded-Graphite-Cloth Laminates

Resin Composition	Forming Pressure	Resin Content Weight Per Cent	Bulk Density g/cc	Young's Modulus 10^6 lbs/in^2	Specific Resistance 10^{-4} ohm-cm	Flexural Strength lbs/in^2
Furfural and Furfuryl Alcohol (1:1)	50	41.1	0.92	0.25	45.8	450
	100	40.2	0.97	0.38	41.5	700
	150	38.4	1.04	0.70	37.3	1510
	200	27.8	1.03	0.80	31.7	210
	250	27.9	1.03	0.83	31.8	530
Furfural and Furfuryl Alcohol (1:1) 5 Weight Per Cent Pitch	50	42.2	0.89	0.24	42.76	500
	100	26.5	0.96	0.56	31.67	900
	150	17.1	0.97	0.54	34.39	720
	200	15.0	0.99	1.38	37.73	700
	250	13.3	1.01	1.48	33.69	620
Furfural and Furfuryl Alcohol (1:1) 10 Weight Per Cent Pitch	50	35.0	0.91	0.38	39.50	880
	100	24.6	0.91	0.45	48.80	730
	150	24.0	0.96	0.71	43.80	990
	200	20.7	0.98	0.66	44.50	600
	250	19.9	0.99	0.69	44.20	660
Furfural and Furfuryl Alcohol (1:1) 15 Weight Per Cent Pitch	50	45.5	0.92	0.37	48.23	650
	100	41.0	0.98	0.36	44.58	870
	150	38.0	1.0	0.51	46.92	1230
	200	36.7	1.0	0.65	47.22	1410
	250	37.6	1.1	0.67	45.55	1440
Furfural and Furfuryl Alcohol (1:1) 20 Weight Per Cent Pitch	50	45.0	0.91	0.28	38.30	900
	100	42.2	0.99	0.41	43.30	1330
	150	37.6	0.97	0.61	45.90	1930
	200	37.7	1.05	0.71	44.50	2170
	250	32.2	1.05	0.83	39.70	2200
Furfural and Furfuryl Alcohol (1:1) 25 Weight Per Cent Pitch	50	49.1	0.92	0.31	45.80	890
	100	41.5	0.97	0.44	41.70	1440
	150	35.1	1.01	0.59	47.70	1950
	200	30.3	1.05	0.70	47.60	2400
	250	31.4	1.09	0.83	44.80	2540

phenolic-bonded laminates. Third, the laminates containing the pitch-resin binder, even those formed at pressures above 150 lbs/in^2, baked and graphitized without delaminating whereas the phenolic-bonded laminates formed at pressures above 150 lbs/in^2 either decreased in strength or delaminated when baked and graphitized. From these observations, it is concluded that the addition of larger quantities of pitch to the liquid

resin should result in laminates with flexural strengths comparable to or better than those of the phenolic-bonded laminates.

3. CARBON-CLOTH COMPOSITES

Significant differences between carbon cloth (baked to approximately 750°C) and graphite cloth were noticed in the early studies utilizing these two materials. Graphite cloth, macerated with a furane-phenolic resin in the ratio of 2:1 (by weight), assumed a moist, fluffy appearance. Carbon cloth, macerated with the same quantity of resin, remained dry and assumed the shape of the container. The surface of the filler material in any carbon composite determines the binder content which, in turn, can influence the strength of the resultant product. Generally speaking, the strength is proportional to the bond carbon content up to the point where excessive gas evolution during pyrolysis of the resin introduces microflaws in the structure.

Samples of rayon cloth were processed to temperatures between 225 and 2800°C. Several properties of these materials were measured. The surface areas of these samples, listed in Table 16 were measured by the BET method[2] and were found to reach a maximum between 600 and 900°C. The surface area was increased by a factor of more than 700 between 225 and 750°C, but was then reduced by a factor of nearly 200 upon graphitization at 2800°C.

Table 16. Effect of Baking Temperature on Surface Area of Rayon Cloth

Baking Temperature, °C	Surface Area, M^2/g
225	0.5
600	445
700	423
750*	405
800	442
900	436
1000	3.5
2800	2.2

* Carbon cloth sample taken from production lot

3.1. Macerated-Carbon-Cloth Composites

A carbon cloth, baked to approximately 750°C, was used as a filler for macerated composites. The cloth was mixed with 50 parts

per hundred of the furane-phenolic resin and reduced to a fibrous mixture by shredding in a bread-type mixer. The macerated carbon cloth-resin mixture was charged to a 9 $^{3}/_{4}$ -inch diameter mold, formed into a plug and cured under a pressure of 750 lbs/in^2 at a temperature of 130°C for 6 hours. Three plugs of this variety, fabricated from carbon cloth, were baked to 800°C and graphitized to 2800°C. Properties of the composite material were measured after each processing step and are given in Table 17. Also tabulated, for comparison purposes, are the properties of a macerated-graphite-cloth composite prepared at the same binder level and processed in a similar manner.*

Table 17. Property Comparison for Macerated-Carbon- and Graphite Composites

Type Filler	Carbon Cloth			Graphite Cloth		
Composite Processing Temp., °C	130	800	2800	130	800	2800
Bulk Density, g/cc	0.96	0.93	0.95	1.26	1.06	0.96
Flexural Strength, lbs/in^2						
w.g.	2240	1400	1850	4900	1400	1000
a.g.	740	880	660	600	900	860
Compressive Strength, lbs/in^2						
w.g.	4070	4150	2150	9100	900	860
a.g.	6000	4610	2460	11000	2700	1600
Young's Modulus, lbs/in^2						
w.g.	0.62	1.00	0.87	1.28	0.67	0.94
a.g.	0.28	0.44	0.36	0.53	0.46	0.52
Specific Resistance, 10^{-4} ohm-cm						
w.g.		337	37.3	300	100	60
a.g.		283	87.9	900	400	90
Weight Loss, Per Cent		18.3	11.3		18.4	3.3
Shrinkage, Per Cent						
w.g.		5.5	5.8		1.6	0.5
a.g.		5.8	5.0		2.8	0.6

* This composite was fabricated prior to the processing refinements but the properties were typical for this material at the time this investigation was performed.

Differences in appearance between carbon- and graphite-cloth composites after baking and graphitizing indicated that an insufficient amount of binder was used in the carbon composite. Macerated carbon cloth (750°C) and resin mixtures were prepared at binder levels of 50, 60, 70 and 80 parts per hundred. Five plugs, 5 inches in diameter and 5 inches in length, were fabricated from these mixtures. The plugs were formed at a pressure of 750 lbs/in^2, cured under that pressure for 6 hours at 125°C, baked to 800°C, and graphitized to 2800°C. Physical properties of the five plugs are shown in Table 18. The flexural strength of the composites formed at binder levels of 60, 70 and 80 parts per hundred were lower than those of the plug formed at 50 parts per hundred but the flexural strength of the plug fabricated at 50 parts per hundred was also much lower than that previously cited in Table 17. The extremely poor strength of these composites was unexpected, since no flaws or cracks had appeared during processing. These poor results were attributed to probable variations in the thermal history of the cloth.

Table 18. Properties of Plugs Used in Binder Level Study for Carbon Cloth

Binder Level		Graphite Properties					
		Bulk Density	Specific Resistance 10^{-4} ohm-cm		Young's Modulus 10^6 lbs/in^2		Flexural Strength lbs/in^2
PPH	Weight Per Cent	g/cc	w.g.	a.g.	w.g.	a.g.	w.g. a.g.
50	33.3	0.92	60.9	12.1	0.89	0.23	1160 215
60	37.5	0.93	63.1	17.6	0.85	0.66	980 122
70	41.2	0.99	44.8	19.4	0.74	0.06	740 50
80	44.5	0.96	46.2	15.4	0.62	0.06	930 132

N = 5 for all entries

Baked and graphitized plugs, formed from carbon cloth at a binder level of 80 parts per hundred, appeared to have a binder deficiency. The difference in appearance between macerated carbon cloth at a binder level of 80 parts per hundred and macerated graphite cloth at a binder level of 50 parts per hundred is illustrated in Figure 16.

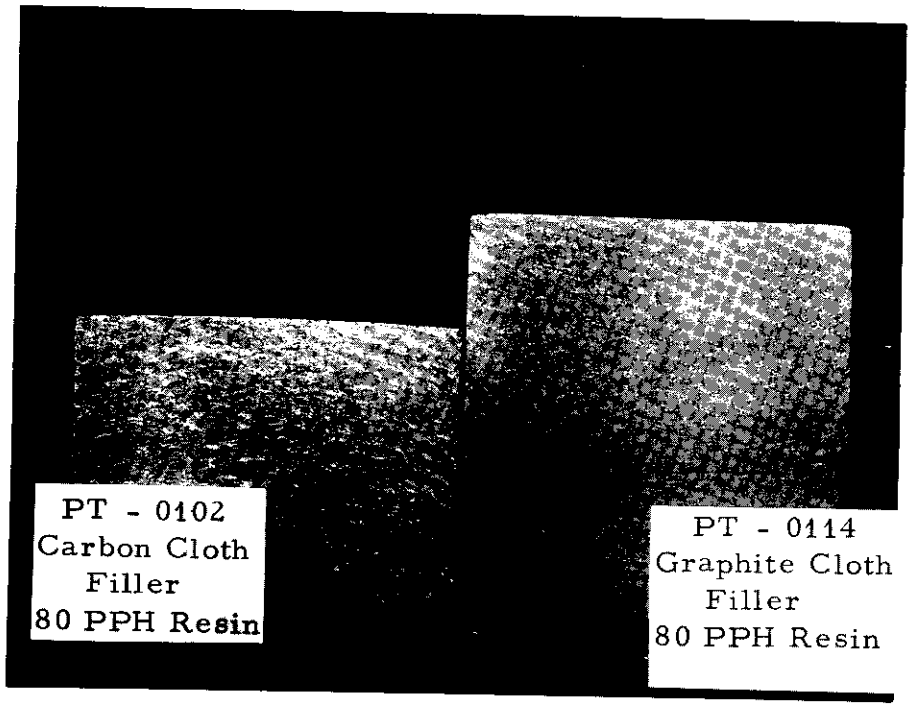


Figure 16. Photograph Illustrating Difference in Appearance of Carbon- and Graphite-Cloth Composites.

Both plugs shown in this figure were formed at a pressure of 750 lbs/in^2, baked to 800°C and graphitized to 2800°C. Additional work in the area of binder levels is needed to explain the unusual characteristics of carbon-cloth composites. All future work should utilize cloth whose thermal history has been closely monitored.

3.2. Carbon-Cloth Laminates

The feasibility of using carbon cloth as a filler for laminated structures was investigated to determine the optimum forming pressure, and to characterize the laminates fabricated at this pressure. The effect of precuring and of carbon-cloth weave on laminate properties was also investigated.

3.2.1. Selection of Forming Pressure for Carbon-Cloth Laminates

Laminates for determining the optimum forming pressure were made from VCA carbon cloth. Strips of this cloth 6 inches wide were resin treated, passed through the squeeze-rolls, spaced 0.015 inch apart, and cut into 5-inch square swatches. Laminates consisting of 45 plies were fabricated at pressures ranging from 36 lbs/in^2 to 300 lbs/in^2 were then baked and graphitized. The resin content measured after curing the laminate, and other properties measured after graphitizing are listed in Table 19.

Table 19. Effect of Forming Pressure on Properties* of Graphitized-Carbon-Cloth Laminates

Forming Pressure lbs/in^2	Cured Resin Content, Weight Per Cent	Bulk Density, g/cc	Flexural Strength lbs/in^2
36	33.5	1.02	2800
100	36.0	1.09	2800
150	31.5	1.08	2900
200	33.3	1.06	3200
300	33.9	1.07	2400

* N = 5 for all properties

All properties measured with the grain

Several conclusions concerning the properties of carbon-cloth laminates were reached by concurrently examining the properties of graphite-cloth laminates discussed in Section 2.2.1. Comparing the cured resin content of carbon- and of graphite-cloth laminates indicated a significant difference between these fillers. Forming pressure had little effect on the resin content of carbon-cloth laminates but the resin content of graphite-cloth laminates decreased with increased forming pressure. This effect is shown clearly in Figure 17 which is a plot

of resin content versus forming pressure.

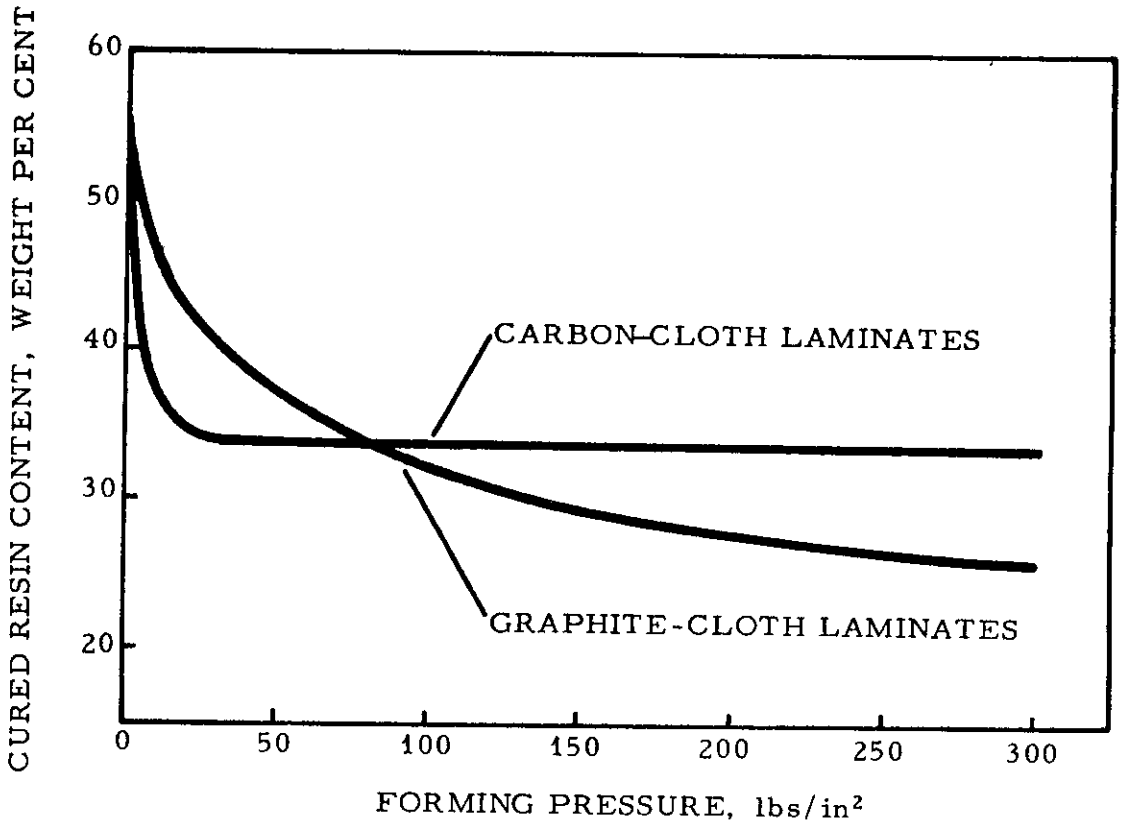
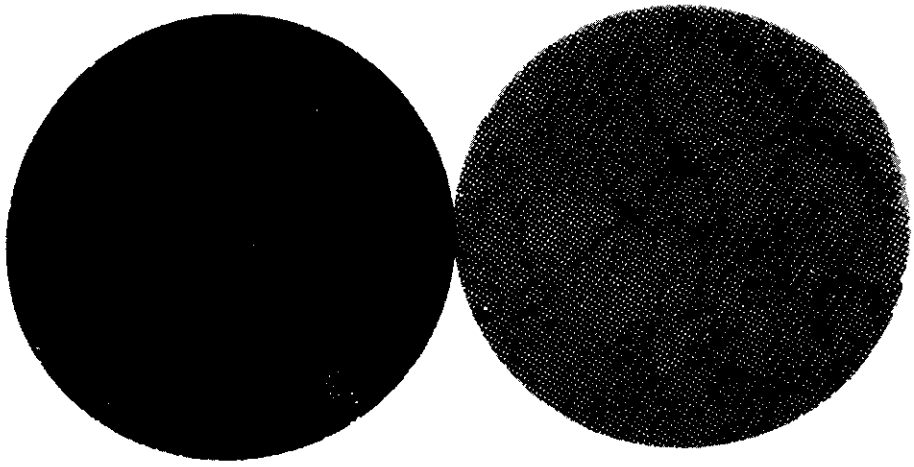


Figure 17. Effect of Forming Pressure on Resin Content of Cured Carbon- and Graphite-Cloth Laminates

Apparently, the resin in this carbon cloth is located around the individual filaments of each fiber. In this graphite cloth, however, the resin is located on the surface of the fibers between the intersection of the warp and the fill. The difference in resin location is shown by the appearance of the carbon- and graphite-cloth swatches in Figure 18. These swatches were impregnated with resin and cured at a pressure of 200 lbs/in^2 and at a temperature of 130°C. The circular disks were cut from the two swatches and examined closely. Although the carbon cloth retained a greater quantity of resin than did the graphite cloth, the carbon cloth appeared more porous, indicating that the resin had been absorbed into the fibers.



Graphite Cloth Carbon Cloth

Figure 18. Swatches of Carbon and Graphite Cloth Demonstrating Difference in Cured Resin Location

The graphs (Figure 19) of flexural strengths versus forming pressures for carbon-cloth laminates (PT-0099) and for graphite-cloth laminates (PT-0111) show that the effect of forming pressure was more pronounced on the graphite laminates. A flexural strength increase of 400 lbs/in^2(2800 lbs/in^2 to 3200 lbs/in^2) was observed when the forming pressure was increased from 50 lbs/in^2 to the optimum of 200 lbs/in^2. Because the carbon cloth absorbed the resin into the fiber filaments as well as on the surface, a nearly continuous phase of resin existed throughout the structure when carbon cloth was formed into laminates, even at low pressures. The more thorough dispersion of the binder, and consequently better bonding, in the carbon-cloth laminates was also

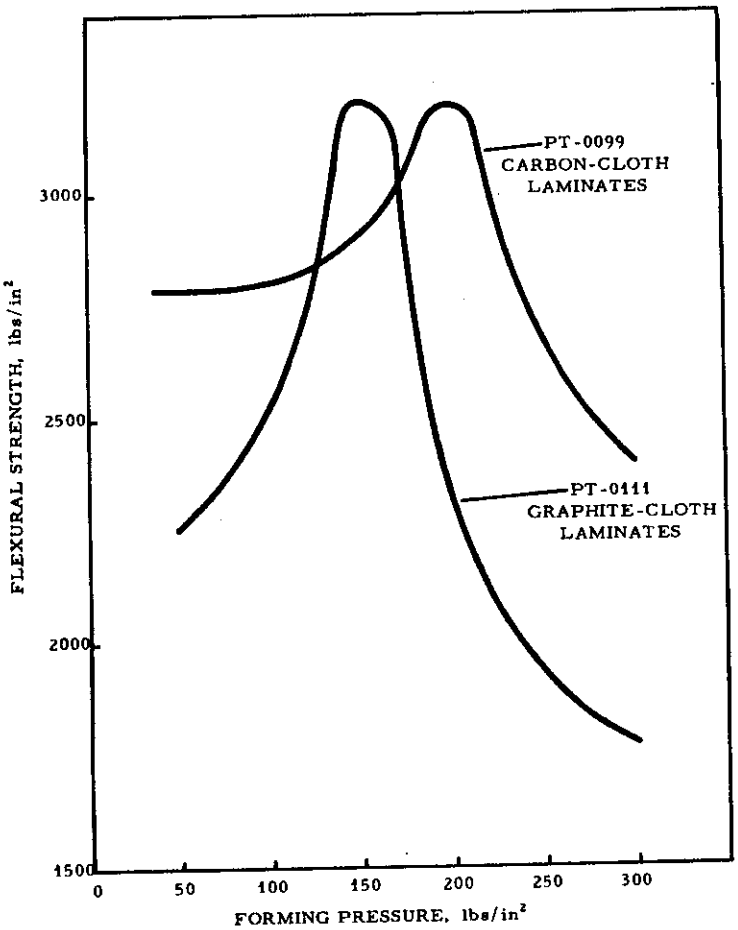


Figure 19. Effect of Forming Pressure on Flexural Strength of Graphitized-Carbon- and Graphite-Cloth Laminates

illustrated by the difference in the appearance between the breaks of carbon-cloth laminates and graphite-cloth laminates after each had been tested for flexural strength. This difference in appearance of the flexural breaks for PT-0111 and PT-0099, each fabricated at its optimum forming pressure, is shown in Figure 20. The fracture of the carbon-cloth laminate (PT-0099) was a relatively "clean" fibrous break and resulted in rupture of all the layers whereas the fracture of the graphite-cloth laminate (PT-0111) resulted in considerable delamination of the layers and not all layers of cloth were ruptured.

The photograph in Figure 20, as did Figure 16, shows the difference in the appearance of PT-0099 and PT-0111. Although the PT-0099 had a cured resin content of 33.5 per cent as compared to 29.4 per cent for the PT-0111, the former, or carbon-cloth laminate,

PT - 0099
Carbon Cloth Laminate

PT-0111
Graphite Cloth Laminates

Figure 20. Comparison of Breaks Occurring in Flexural Specimens of Cloth Laminates

appeared to have an insufficient amount of binder in contrast to the PT-0111, or graphite-cloth laminate.

Results of the studies reported in this section led to the conclusion that optimum forming pressures for carbon- and graphite-cloth laminates were about 200 and 150 lbs/in^2, respectively. The forming pressure was higher for the carbon-cloth laminates because the additional pressure did not appreciably reduce the resin content of the impregnated cloth and the greater quantity of resin available for bonding permitted the higher pressures to be used without breakdown of the fibers. In the graphite-cloth laminates, the fibers were in intimate contact at 150 lbs/in^2 and additional pressure reduced the resin content

to a point where inter-lamina bond strengths were lowered.

3.2.2. Precuring Carbon Cloth for Laminate Strength

The technique of precuring was also investigated as a method of strength improvement for carbon-cloth laminates. This study, as described for graphite laminates in Section 2.2.4, consisted of precuring the resin impregnated carbon cloth for periods of 1, 2, 3, 4 and 5 minutes in an air-circulating oven preset to 100°C ± 5°C. The carbon cloth precured for each of the above times was then fabricated into 5 laminates at a pressure of 200 lbs/in^2 and baked to 800°C. Laminates using the cloth precured for 2, 4 and 5 minutes delaminated in the bake but the remaining two laminates were graphitized to 2800°C and used for physical property measurements.

The cured resin content, graphite bulk density and flexural strength of the flaw-free laminates are listed in Table 20.

Table 20. Effect of Precuring on the Strength of Carbon-Cloth Laminates

Precure Time, lbs/in^2	Cured Resin Content, Weight Per Cent	Bulk Density g/cc	Flexural Strength lbs/in^2
1	31.3	1.12	2600
3	32.3	1.12	2700

N = 5 for all entries

The flexural strength of these laminates was 15 to 18 per cent lower than that of conventional carbon-cloth laminates. No further work in this area was recommended because of the low strength and poor baking qualities of laminates produced from precured carbon cloth.

3.2.3. Effect of Carbon-Cloth Weave Structure on the Flexural Strength of Laminates

The use of twill weave, rather than square weave, carbon cloth has been evaluated as a method for improving the flexural strengths of

carbon-cloth laminates. This study utilized a regular twill weave cloth, grade VCH.

Laminates for evaluating VCH filler were fabricated according to the method for making the graphite-cloth laminates described in Section 2.2.4. Pressures of 12.5, 25, 50 and on up to 300 lbs/in^2 in 50 pound increments were used for forming the laminates. Physical properties of these laminates, shown in Table 21, indicated that the optimum forming pressure was approximately 50 lbs/in^2 which resulted in graphite flexural strengths of 2700 lbs/in^2. These strength values are about 15 per cent lower than those of VCA carbon-cloth laminates formed at their optimum pressure of 200 lbs/in^2. The optimum forming pressure for the VCH twill weave cloth is much lower than that for VCA square weave cloth because the reduced crimp of the former requires less pressure to effect intimate contact between the fibers.

Table 21. Effect of Forming Pressure on the Properties* of VCH Carbon-Cloth Laminates

Forming Pressure, lbs/in^2	Cured Resin Content Weight Per Cent	Bulk Density g/cc	Flexural Strength lbs/in^2
12.5	----	1.04	1780
25	----	1.08	2250
50	35.5	1.11	2700
100	32.9	1.07	1430
150	----	1.04	1600
200	31.0	1.06	1340
250	30.0	1.07	1640
300	31.0	1.04	1440

* N = 5 for all entries.
All properties measured with the grain

4. HEAT-TREATED-CLOTH COMPOSITES

4.1. Relative Shrinkage Rates of Binder and Heat-Treated Cloth

A second factor affecting the strength of carbon and graphite composites is the difference in the rates with which the filler and binder materials shrink during the baking and graphitizing operations. For example, pregraphitized filler material experiences no shrinkage while the composite is undergoing graphitization, and the differential shrinkage between the filler material and the binder will be a maximum. Under such conditions, stresses can be induced which result in bond failures and subsequent low strengths in the finished product.

An investigation into the relative shrinkage of the components in the cloth resin system was undertaken to determine if improvement in strength could be made. It was theorized that maximum strength of the composite would be realized when the heat-treatment temperature of the cloth filler was such that its residual shrinkage, upon graphitization, just matched that of the resin binder. To determine this temperature, the area change of cloth samples was measured as a function of heat-treatment temperature up to 2900°C. The lineal shrinkage of the resin, after thermosetting, was then determined by measuring its weight loss and change in pycnometric density over the same temperature range. Figure 21 compares the lineal shrinkage curves of raw, heat-treated and graphitized cloth, and resin as a function of processing temperature.

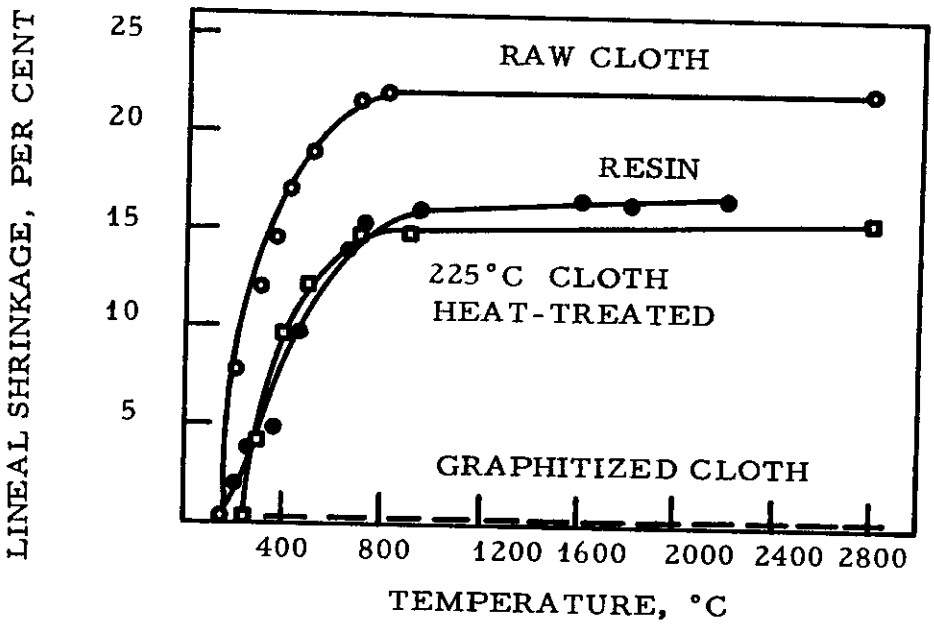


Figure 21. Lineal Shrinkage of Raw, Heat-Treated, and Graphitized Cloths and Resin versus Processing Temperature

As can be seen from these curves, the raw cloth shrank more than the resin, and the graphite cloth had no shrinkage up to 2800°C. Figure 21 shows also that cloth heat treated to a temperature of 225°C had a residual shrinkage very close to that of the resin indicating that the differential shrinkage in a composite made from 225°C heat-treated cloth and resin would be low.

4.2. Macerated-Heat-Treated-Cloth Composites

The effects of the low differential shrinkage between binder and filler on the strength of cloth composites was investigated by forming plugs 3 inches in diameter by 3 inches in length from macerated cloth (grade WC-0075) which had been heat treated to 225°C. The plugs were cured, baked, graphitized in the usual manner and cut into specimens for physical property measurements. Table 22 lists the properties of these composites and compares them with those of identically processed composites made with carbon and graphite cloth. The fourfold or greater increase in flexural strength which resulted from the use of 225°C heat-treated cloth demonstrated the improvement in structural integrity brought about by minimizing the differential shrinkage between the filler and binder materials.

Table 22. Effect of Heat-Treatment Temperature of Base Cloth Material on Physical Properties* of Macerated-Graphite-Cloth Composites

Heat-Treatment Temperature of Base Cloth, °C	225	750	2800
Weight Loss, 150-2800°C, Per Cent	52.2	23.7	16.5
Volume Shrinkage, 150-2800°C, Per Cent	56.5	22.2	10.0
Bulk Density, g/cc	1.39	1.02	1.13
Electrical Resistivity, 10^{-4} ohm-cm	36.00	35.00	42.00
Flexural Strength, lbs/in^2	8300	2000	1700
Young's Modulus, 10^6 lbs/in^2	2.50	0.94	0.92
Specific Strength, inches	165,000	54,500	41,700

* All properties measured on with-the-grain specimens

The extremely high shrinkage encountered by the heat-treated-cloth composite also changed the structure. The photomicrographs of heat-treated (Figure 22) and graphite-cloth (Figure 23) composites illustrate the structure of the two materials and show that the heat-treated-cloth composite had undergone such high shrinkages in processing that it no longer had the appearance of a fibrous material.

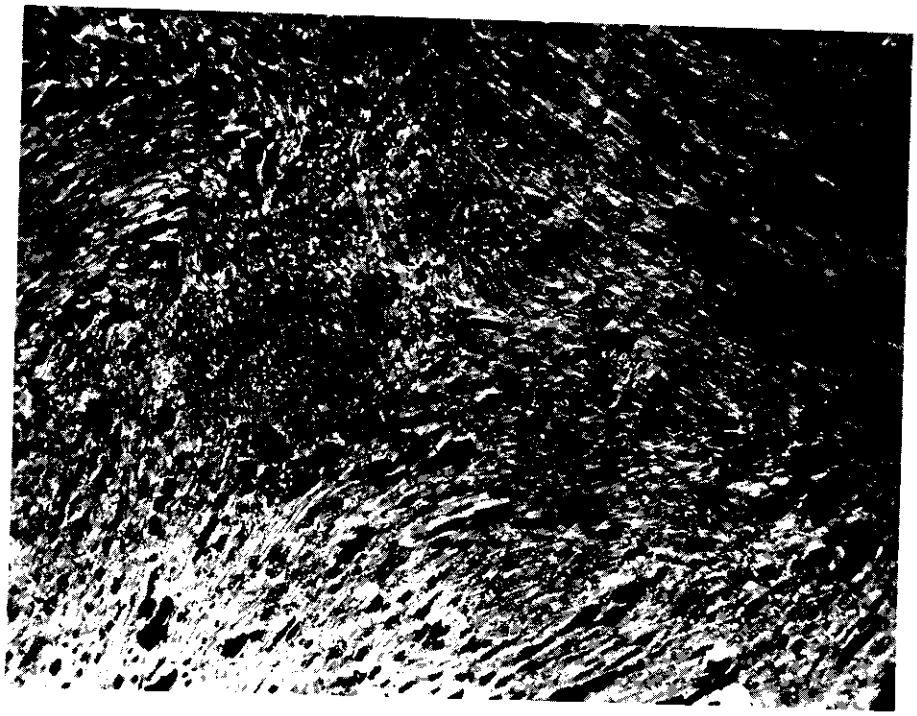


Figure 22. Photomicrograph of Macerated-Heat-Treated-Cloth Composite After Graphitization, With the Grain, 100X

Figure 23. Photomicrograph of Macerated-Graphite-Cloth-Composites After Graphitization, With the Grain, (100X)

Additional trials to scale up to composite sizes larger than 3-inch diameter plugs with macerated-heat-treated cloth as the filler have thus far been unsuccessful because of the formation of cracks during the baking operation. The cracking was caused by the excessive shrinkage as shown in Table 22. A 56.5 per cent volume shrinkage occurred from the cured to the graphitized state, and most of it occurred during the 200 to 800°C interval. Slight temperature gradients in the article during this period of maximum shrinkage set up stresses great enough to cause the piece to crack. As the size of the article increased, the effect became more severe.

4.3. Heat-Treated-Cloth Laminates

Fabrication of heat-treated-cloth laminates was investigated but cracking problems were encountered similar to those for the composites made from macerated cloth (see Section 4.2). Approximately 12 forming trials were made and only 2 laminates were produced that were without cracks. Another laminate (Figure 24) contained only one crack and this crack was not characteristic for laminates since it occurred across the layers. The properties of the three laminates, one formed at 50 lbs/in^2 pressure from 225°C heat-treated cloth, and one each at pressures of 100 and 150 lbs/in^2 from 400°C heat-treated

cloth are given in Table 23.

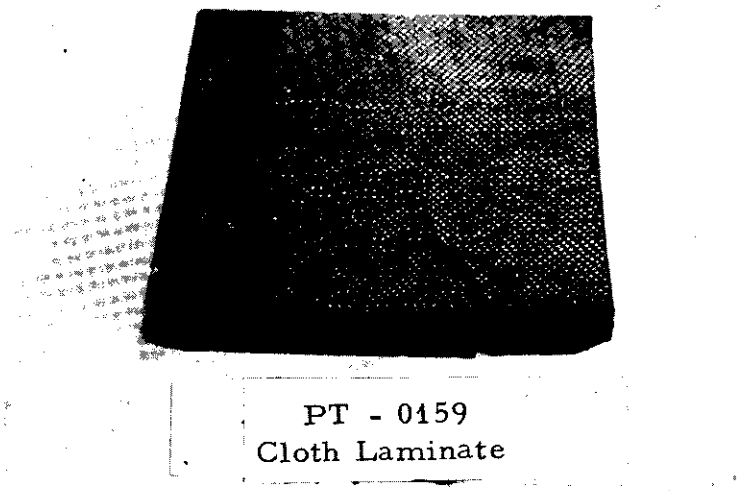


Figure 24. Photograph of Graphitized Laminate of 225°C Heat-Treated Cloth

Table 23. Graphite Properties* of Heat-Treated-Cloth Laminates

Type Filler	225°C H. T.**	~ 400 °C H. T.**	
Forming Pressure, lbs/in^2	50	100	150
Bulk Density, g/cc	1.32	1.26	1.27
Flexural Strength, lbs/in^2 w.g.	3750	4670	6500
Sonic Modulus, 10^6 lbs/in^2 w.g.	2.15	2.20	2.36

* N = 3 for all entries
** H. T. = Heat treating temperature of filler

The results of these trials demonstrated that high-strength laminates could be formed and processed from heat-treated cloth. Brittleness of the laminates and the difficulties in processing, however, make heat-treated cloth an impractical material for this use.

5. CARBONACEOUS-FELT COMPOSITES

The search for new fillers to give fibrous composites unique or improved properties was extended to include carbonaceous felts. Felt is a nonwoven material consisting of matted fibers. Two characteristics of the felts which could result in unusual properties are the random orientation of the matted fibers and the felt nap. Carbonaceous felts are available commercially in the carbon form (grade VDF) and the graphite form (grade WDF). The raw materials for these grades are identical and the processing procedures are analogous except for the final temperature. Carbonaceous felts were evaluated primarily as a filler in laminates. Scale up problems, however, necessitated additional feasibility studies with both macerated- and diced-felt structures.

5.1. Carbonaceous-Felt Laminates

Preliminary trials to evaluate carbonaceous felts as a filler were concerned with felt laminates. Grade VDF carbon felt and grade WDF graphite felt were evaluated as filler materials for felt laminates. Fabrication of felt laminates was similar to that outlined for cloth laminates. This method consisted of dipping the felt in a furane-phenolic resin, passing the impregnated felt through a squeeze-roll, and forming it under pressure and temperature into a multilayer laminate. The laminates were then baked and graphitized to yield a thermally-stable material.

5.1.1. Selection of Filler, Binder and Forming Pressure for Felt Laminates

Fabricating cloth composites which are structurally sound depends on finding a workable forming pressure. The inherent properties of carbonaceous felts, especially of graphite felt, necessitate a consideration of three variables in the processing of laminates; type of filler, type of binder, and forming pressure. All of these parameters are in turn influenced by the tensile strength of the felt.

Selection of filler type, VDF carbon felt or WDF graphite felt, was facilitated by the inability of the graphite felt to withstand the resin distribution step. When the resin saturated graphite felt was passed through the stainless steel squeeze-rolls spaced 0.040 inch apart, the mechanical action tore the felt, making it unusable as a filler for laminates. The strength of carbon felt also was impaired by the resin-impregnating process and the poor impregnating characteristics of both materials were attributed to their low tensile strength.

Properties of these filler materials, shown in Table 24, indicated that graphite felt had approximately one-half the tensile strength of carbon felt.

Table 24. *Properties of Carbonaceous Felts

Type	750 VDF	2800 WDF
Processing Temperature, °C		
Grade		
Weight, oz/yd^2	10.5	10.6
Permeability, ft^3/min/ft^2 at 0.5 in H_2O P	65	60
Tensile Strength, lbs.		
** W	3	1.5
***F	3	1.0
Electrical Resistance, ohm/in^2		
W	-	0.5
F	-	0.6
Thermal Conductivity, BTU/hr ft^2/°F/ft	0.02	

* NCC Advanced Technical Information Bulletin No. 104 HJ
** W - Warp
*** F - Fill

To alleviate the impregnating problem, a resin of lower viscosity was employed consisting of 33 weight per cent powder-phenolic dissolved in 67 weight per cent acetone. Evaporation of the acetone after resin treating the felt left a uniform coat of phenolic which imparted additional strength to the felt. Although this change solved the resin treating problem, application of heat in the forming process reduced the felt to its original tensile strength. When the applied forming pressure exceeded the tensile strength of the felt, the laminate ruptured. Allowable forming pressures were approximately 75 lbs/in^2 for graphite felt and 200 lbs/in^2 for carbon felt.

As a result of these observations, further work using felt as a filler for laminates was restricted to carbon felt with the low viscosity resin system consisting of phenolic dissolved in acetone. Forming pressures were less than 200 lbs/in^2. Special emphasis was placed

on fabricating structurally sound laminates for property characterization.

5.1.2. Fabrication and Characterization of Carbon-Felt Laminates

The initial property characterization on VDF carbon-felt laminates was performed on a 7-inch square by 1-inch thick piece. The felt for producing this laminate was cut into 7-inch squares and dipped into a solution containing 67 per cent acetone and 33 per cent phenolic. The resin-treated-felt swatches were individually passed through a squeeze-roll separated approximately 0.040 inch, and air dried to remove the acetone. Thirty-five layers of the resin treated felt were stacked into forming position on the 10-ton bench press. The high compression ratio (8 inches felt to 1 inch laminate) necessitated careful stacking to prevent buckling. The laminate was cured between the electrically heated platens of the press at 130°C under a pressure of 175 lbs/in^2. The laminate was baked and graphitized to 800 and 2800°C, respectively.

Test samples were cut from the laminate in the cured (PT-0031), baked (PT-0032), and graphitized (PT-0033) forms, physical properties were measured on the samples and the results are shown in Table 25.

Table 25. Properties* of VDF Carbon-Felt Laminates

Final Processing Temperature of Laminate	130°C	800°C	2800°C
Grade	PT-0031	PT-0032	PT-0033
Bulk Density, g/cc	1.15	1.0	0.72
Flexural Strength, lbs/in^2			
w.g.**	12,600	2,290	3,400
Compressive Strength, lbs/in^2			
a.g.***	20,920	6,170	3,500
w.g.	21,500	6,070	4,900
Young's Modulus, 10^6 lbs/in^2			
w.g.	0.88	0.85	1.16
Specific Resistance, 10^{-4} ohm-cm		0.29	17
Weight Loss, Per Cent		28.4	11.5
Shrinkage, Per Cent			
w.g.		3.5	
a.g.		7.6	

* N = 3 for all entries
** w.g. = with the grain
*** a.g. = across the grain

The most significant of the properties were the high flexural strength and the low density and, especially, the increase in strength from carbon to graphite. This laminate displayed also, an unusual isotropy of compressive strength which was probably caused by the random orientation of the matted fibers and the felt nap. With-the-grain and across-the-grain photomicrographs demonstrating the random orientation of the fibers in PT-0033 are shown in Figures 25 and 26.

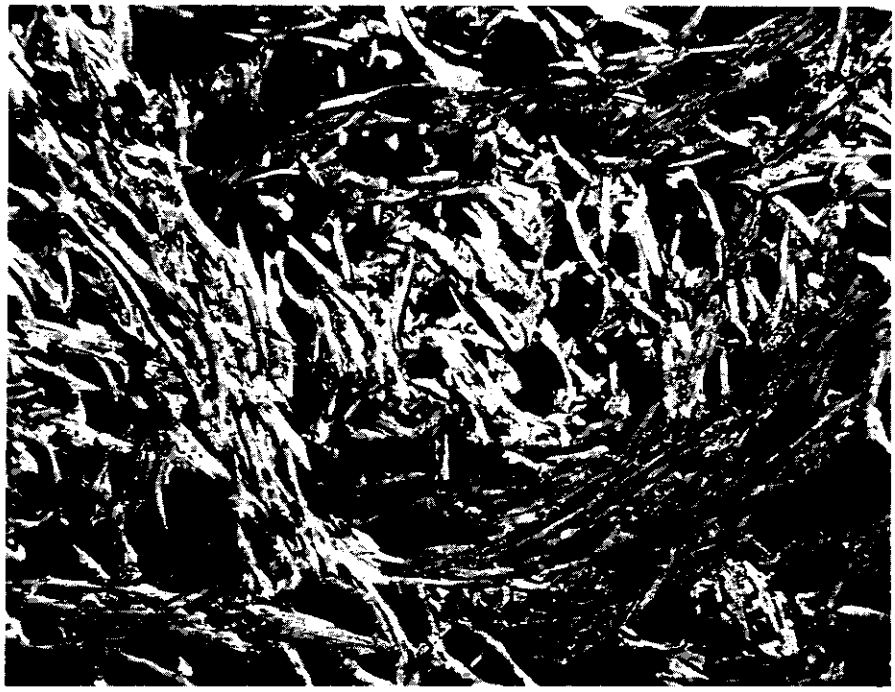


Figure 25. Photomicrograph of PT-0033 Illustrating Random Orientation of Fibers in With-the-Grain Direction

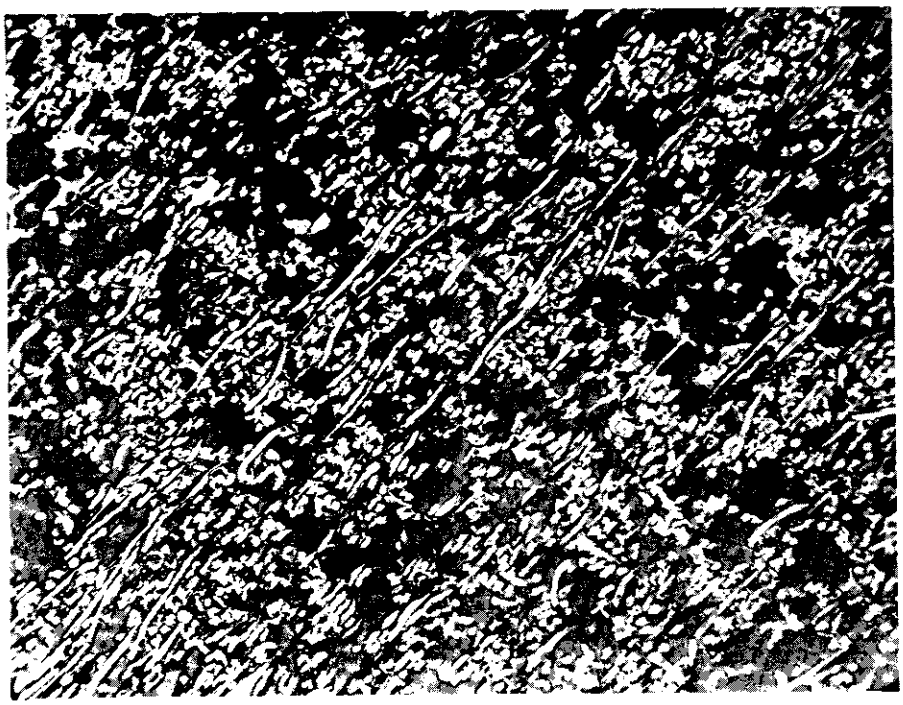


Figure 26. Photomicrograph of PT-0033 Illustrating Random Orientation of Fibers in Across-the-Grain Direction

The properties of carbon-felt laminates shown in Table 25 make these materials look extremely promising but measurements on a small number of samples from a single laminate could be somewhat misleading. To determine whether these properties were reproducible, another characterization was conducted on four laminates. Processing procedures were analogous to the method used for fabricating the single laminate previously described. Properties of the four laminates are shown in Table 26. The properties did not differ greatly from those given in Table 25 with the exception of bulk densities which averaged approximately 14 per cent higher for the four laminates than for the single piece.

The significance of these two trials is that carbon-felt laminates can be fabricated and processed to yield high-strength and low-density

Table 26. Properties of Carbon-Felt Laminates

Piece	A			B			C			D		
Grade	PT-0031	PT-0032	PT-0033	PT 0031	PT-0032	PT-0033	PT-0031	PT-0032	PT-0033	PT-0031	PT-0032	PT-0033
Curing Time, Hrs.	2.9			3.5			3.0			3.0		
Resin Content	---			49.7			43.2			55.0		
Bulk Density, g/cc	1.17	0.99	0.95	1.11	0.99	0.94	1.13	1.02	0.97	1.10	0.99	0.96
Flexural Strength, lbs/in^2												
w.g.	11,870	4,760	3,290	11,350	2,320	3,090	12,800	2,180	2,790	12,950	1,740	3,295
Compressive Strength, lbs/in^2												
w.g.	23,500	5,080	4,070	24,300	3,960	3,260	25,200	3,490	3,060	24,900	4,870	3,240
a.g.	25,500	4,510	6,920	24,400	5,900	5,090	25,600	4,850	3,990	24,300	5,980	4,650
Specific Resistance, 10^{-4}ohm-cm												
w.g.	345,000	1,360	40	342,000	1,550	30	2,000,000	1,760	20	1,270,000	1,750	20
Young's Modulus, 10^6 lbs/in^2												
w.g.	0.878	1.01	1.30	0.88	0.95	1.15	0.87	0.88	1.04	0.94	1.02	1.05
Specific Strength, Inches	281,940	133,700	96,200	283,750	65,170	91,420	314,500	59,370	71,346	327,020	48,880	95,500

materials. Although these characterizations were made on small laminates, it was proved that the properties are reproducible. Additional trials were necessary to determine the feasibility of scale up to large sizes.

5.1.3. Scale Up of Felt Laminates

Initial scale-up trials were made in an effort to form felt laminates 9 $^{3}/_{4}$ inches in diameter by 3 $^{1}/_{2}$ inches in thickness. In an effort to prevent buckling, the trials were made in an enclosed mold, all parts of which were electrically heated, and the temperature was controlled with thermo-switches. The felt was resin treated, air-dried, and stacked into the mold cavity. The first two attempts failed to produce laminates without delaminations. Exudation of binder during the early curing stages trapped the polymerization gases in the laminate and prevented their gradual escape. When the laminate was stripped from the mold, internal pressure set up by these entrapped gases caused delaminations.

The next scale-up trials were performed without the use of an enclosed mold and the platens were heated electrically to supply the heat for curing. Three trials with this forming method produced two cured laminates 9 $^{3}/_{4}$ inches in diameter by 2 $^{1}/_{2}$ inches in thickness which were without visible flaws. Because of the column effect, however, the forming pressure had to be reduced from 174 lbs/in^2 to 150 lbs/in^2 and large variations occurred in the cured PT-0031 properties as shown in Table 27. The wide variation in strength was probably caused by non-uniform forming pressure due to column effect.

Table 27. *Properties of PT-0031 Felt Laminates

Grade	PT-0031	PT-0031
Trial Number	2	3
Bulk Density, g/cc	1.18	1.08
Flexural Strength, lbs/in^2		
** w.g.	4,800	7,500
Compressive Strength, lbs/in^2		
*** a.g.	17,300	16,100
w.g.	41,000	15,200
Young's Modulus, 10^6 lbs/in^2	0.84	0.79

* N = 5 for all entries
** w.g. = with the grain
*** a.g. = across the grain

In an effort to attain even higher strengths, a laminate was fabricated from VDF carbon felt. The raw material used for producing grade VDF was a rayon felt containing an insert of 2 by 2 basket weave cloth and is referred to as an inserted felt. The laminate formed from VDF was fabricated as previously described at a pressure of 150 lbs/in^2. The cured properties of the inserted-felt laminate (PT-0091) are compared with those of a similarly processed PT-0031 laminate in Table 28. As seen in this table, the inserted felt produced stronger cured laminates, and, because of the improved tensile strength, higher forming pressures probably could be used if necessary.

Table 28. Property Comparison for Cured Laminates of VDF Carbon Felt (PT-0031) and VDF Inserted Carbon Felt (PT-0091)

Grade	PT-0091	PT-0031
Bulk Density, g/cc	1.13	1.08
Flexural Strength, lbs/in^2		
w.g.	10,400	7,500
Compressive Strength, lbs/in^2		
a.g.	21,300	16,100
w.g.	16,000	15,200
Young's Modulus, 10^6 lbs/in^2		
w.g.	1.02	0.79

After most of the problems in curing had been solved, additional problems were encountered in baking and graphitizing felt laminates of the larger size. The poor baking qualities of these laminates seem to stem from a combination of three factors; extremely high resin content of the laminate (49-55 weight per cent), stresses caused by nonuniform pressure during forming, and variations in original thermal history of the filler. Although most of the laminates cracked in baking, several baked (PT-0032) and graphitized (PT-0033) pieces were produced successfully.

5.2. Diced-Felt Composites

Large-carbon-felt laminates were extremely difficult to process in sections without flaws. The column effect encountered during forming because of the stacked layers resulted in nonuniform pressure distribution, which induced stresses in the laminate, and limited the thickness of the laminate which could be produced by this process. Because of

these problems, new methods for using the felt as filler were investigated. One method explored was the use of diced felt.

The preliminary work on diced-felt composites was to establish an optimum forming pressure. Carbon felt and graphite felt were diced into 1-inch squares and treated with a resin consisting of 25 weight per cent phenolic and 75 weight per cent acetone. The resin-treated felt was formed into 3-inch diameter by 3-inch length plugs at pressures ranging from 200 to 800 lbs/in^2. At the 800 lbs/in^2 pressure, the felt began to extrude around the mold punches. The cured plugs were baked, sectioned and examined and all samples were found to be extensively cracked. Because of the poor success of this initial trial no further work with diced-felt structures was attempted. The cured bulk densities of these plugs are shown in Table 29.

Table 29. Cured Bulk Density of Diced-Carbon- and Graphite-Felt Diced Composites

Type Filler	Carbon-Felt			Graphite-Felt		
Forming Pressure, lbs/in^2	200	400	600	200	400	600
Bulk Density, g/cc	1.27	1.28	1.30	0.98	1.24	1.30

5.3. Macerated-Carbon-Felt Composites

Another method for using felt as a filler material was to macerate the carbon felt. Maceration of the felt with the furane-phenolic binder was accomplished by a one-step mixing operation in a bread type mixer. A weighted lid was used on the mixer to facilitate contact of the mix with the blades. An attempt was made to establish an optimum forming pressure by forming plugs 5 inches in diameter by 5 inches in length at pressures ranging from 250 to 750 lbs/in^2. The cured, baked and graphitized properties for the plugs are listed in Table 30. The results do not warrant further evaluation of macerated-carbon-felt forms.

Table 30. Macerated-Carbon-Felt Composite Data

Felt to Binder Ratio	2/1	2/1	2/1	1/1	1/1	1/1	2/3	2/3	2/3
Curing Temperature, °C	175								
Curing Time, hrs.	4								
Curing Pressure, lbs/in^2	250	500	750	250	500	750	250	500	750
PT-0030 Bulk Density, g/cc								0.86	
PT-0030 Flexural Strength, lbs/in^2	Cracked	"	"	"	"	"	"	930	Cracked
PT-0030 Young's Modulus, 10^6 lbs/in^2								0.331	

5.4. Investigation of the Thermal History of Carbonaceous Felts

The effect of controlling the original thermal history of carbonaceous felts on the properties and processing qualities of felt composites was investigated.

5.4.1. Effect of Heat Treating on Shrinkage, Weight Loss, and Coking Value of Rayon Felt

Previous investigation indicated that controlled heat treatment of rayon cloth resulted in a stronger carbonized product.[3] The oxygen-rayon reaction is exothermic, and combustible gases are evolved at approximately 230°C. The temperature of heat treatment, therefore, was limited to about 220°C. The felt was checked for loss of weight and change in area at various times up to 120 hours of heat treatment. The resulting weight losses and shrinkages are given in Table 31 and plotted in Figure 27.

Table 31. Weight Loss and Area Shrinkage of Rayon Felt During 220°C Heat Treatment

Heat Treat Time, Hrs.	Per Cent Area Shrinkage	Per Cent Weight Loss
2	2.8	20.5
4	3.6	27.1
6	4.4	32.6
8	5.2	36.5
16	16.6	52.9
24	24.9	61.0
32	26.9	61.8
48	35.7	67.1
72	45.4	74.1
120	48.6	76.6

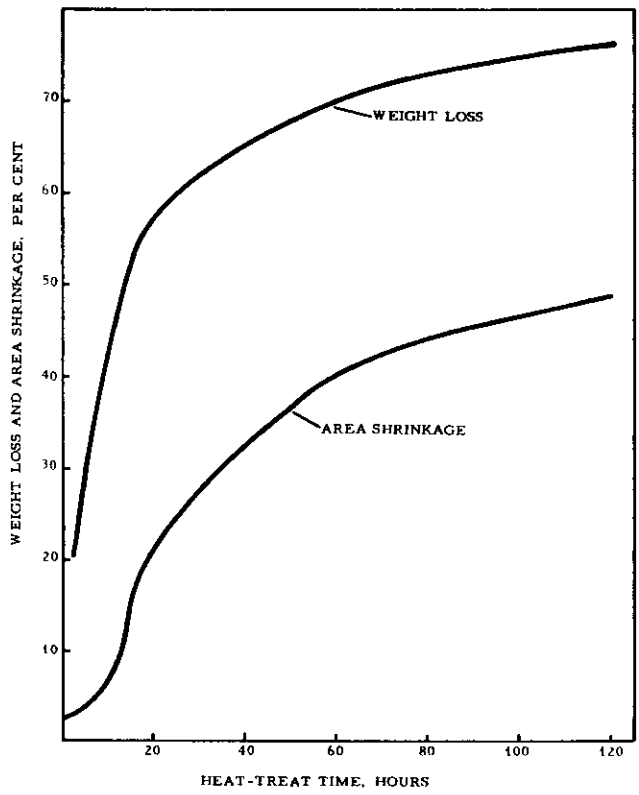


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Figure 27. Weight Loss and Area Shrinkage of Rayon Felt During Heat Treatment at 220°C

Felts which had been heat treated for 0, 2, 4, 6, 8, 16, and 24 hours were selected for further investigation. These heat-treated felts were baked, weighed, and measured at 300°C, 500°C, and 1000°C. The shrinkages and weight losses for the 1000°C baked felts are summarized in Table 32. Coking values resulting from various heat treatments of felts after baking to 1000°C are plotted in Figure 28 and show that the maximum coking value was realized when the felt was heat treated from 6 to 10 hours.

Table 32. Weight Losses and Area Shrinkages of Various Heat-Treated Felts After Baking to 1000°C

Heat Treat Time, Hrs.	1000°C Weight Loss		1000°C Area Shrinkage	
	Per Cent from Raw	Per Cent from Heat Treat	Per Cent from Raw	Per Cent from Heat Treat
0	80.9		43.5	
2	78.4	72.8	45.2	41.2
4	77.4	69.0	42.4	40.3
6	76.7	65.5	44.3	41.9
8	77.1	64.0	43.3	40.2
16	78.7	54.7	47.2	36.7
24	81.4	51.3	50.0	33.4

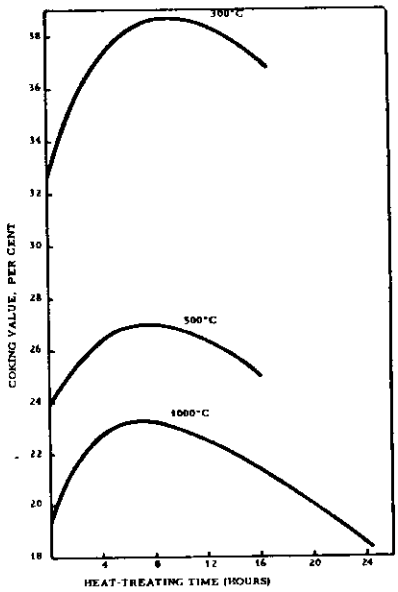

Figure 28. Coking Value of Rayon Felt at Different Baking Temperatures as Related to Curing Time at 220°C

5.4.2. Surface Area Measurements for Carbon Felts With Various Thermal Histories

Samples of felt were prepared at 600°C, 800°C, 900°C, and 1000°C and contained carbon deposit which was condensed from the volatile gases. This carbon deposit probably influenced the surface area measurements and resulted in low values. Apparently, the maximum surface area of carbon felt was developed in the 600 to 800°C range and with a peak indicated at 750°C. The results of the surface area measurements are shown in Table 33.

Table 33. Surface Area of Raw and Carbonized Felts

Baking Temperature °C	Surface Area m^2/g
Raw	0.70
600	291.0
750	412.0
800	0.20
900	0.80
1000	0.20
1340	2.74
2050	2.08
2800	2.13

5.4.3. Electrical Resistivity as a Method for Checking the Carbonization Temperature of Baked Felt

In the processing of conventional carbon and graphite, an increase in processing temperature results in a decrease in electrical resistance. An attempt was made to relate this behavior to a control method for measuring the carbonizing temperatures of carbon felt. Strips of felt, carbonized at temperatures in the 600 to 1000°C range, were checked for electrical resistance. The felt samples, of identical size, were measured for electrical resistance across the 3-inch span between two contact clamps which were mounted on an electrically-nonconducting plate and connected to a resistance meter. The results of this trial are summarized in Table 34 which gives the resistance in ohms per square inch of felt area. Figure 29 is a plot of electrical resistance versus baking temperature.

Table 34. Electrical Resistance of Felts Baked at Various Temperatures

Felt Baking Temperature, °C	N	Electrical Resistance ohms/in² Max.	Min.	Ave.
600	8	42,000	10,000	26,000
700	6	270	100	160
800	6	5.5	3.9	4.6
900	5	3.9	2.5	3.0
1000	5	1.5	1.0	1.2

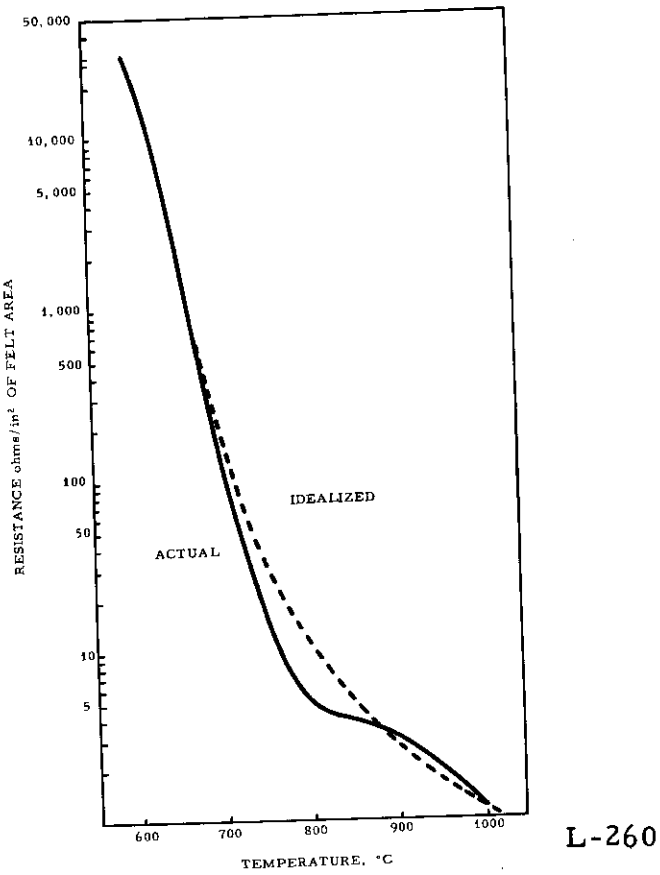

Figure 29. Electrical Resistance of Felt as a Function of the Carbonizing Temperature

The importance of being able to measure and control the baking temperature of felt was illustrated by the wide variation in properties of graphitized-carbon-felt laminates (PT-0033) made from felt fillers whose original carbonization temperatures had varied from 600 to 1000°C. The properties of these laminates are listed in Table 35 and are plotted in Figure 30.

Table 35. Flexural Strengths of Graphitized Laminates Using Felts Baked to Various Temperatures

Temperature, °C	N	Ave. Young's Modulus 10^6 lbs/in^2	Ave. Flexural Strength lbs/in^2
600	5	1.083	3030
700	5	0.829	2630
800	5	0.611	1570
900	5	0.611	1550
1000	5	0.548	1220

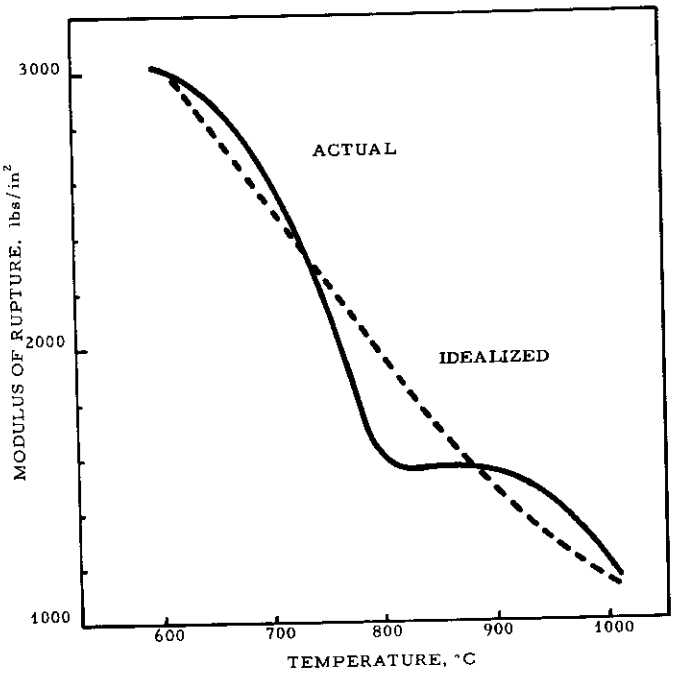

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Figure 30. Flexural Strength of PT-0033 as a Function of the Felt Carbonizing Temperature

5.4.4. Relative Shrinkage Rates of Binder and Heat-Treated Felt

The relative shrinkage rates of carbonized felt and binder have a marked effect on the properties of a laminate formed from these materials. Lineal shrinkage was measured at various carbonizing temperatures for raw felt and for 8-hour heat-treated felt (see Section 5.4.1.) By determining the weight loss and bulk density of the furane-phenolic binder at different carbonizing temperatures, the volumetric shrinkage of the binder was computed. The assumption was made that the shrinkage in all directions was equal and the lineal shrinkage of the binder was calculated. The shrinkage values as a function of temperature for the felt and binder are listed in Table 36 and shown graphically in Figure 31. The shrinkage curves, above 300°C, tended to be parallel and indicated that cracking of the laminates caused by differential shrinkage should not occur at temperatures above 300°C.

Table 36. Shrinkage of Binder and Filler versus Temperature

Carbonizing Temperature, °C	Per Cent Lineal Shrinkage		
	8 Hour Heat Treated Rayon Felt	Raw Rayon Felt	Binder
200			1.5
300	12.5	10.0	2.8
400	19.5		6.7
500	21.0	19.5	10.5
600	24.0		14.0
700	24.6	23.4	20.0
800	26.4	25.5	20.1
900			20.6
1000	26.5	25.5	20.7

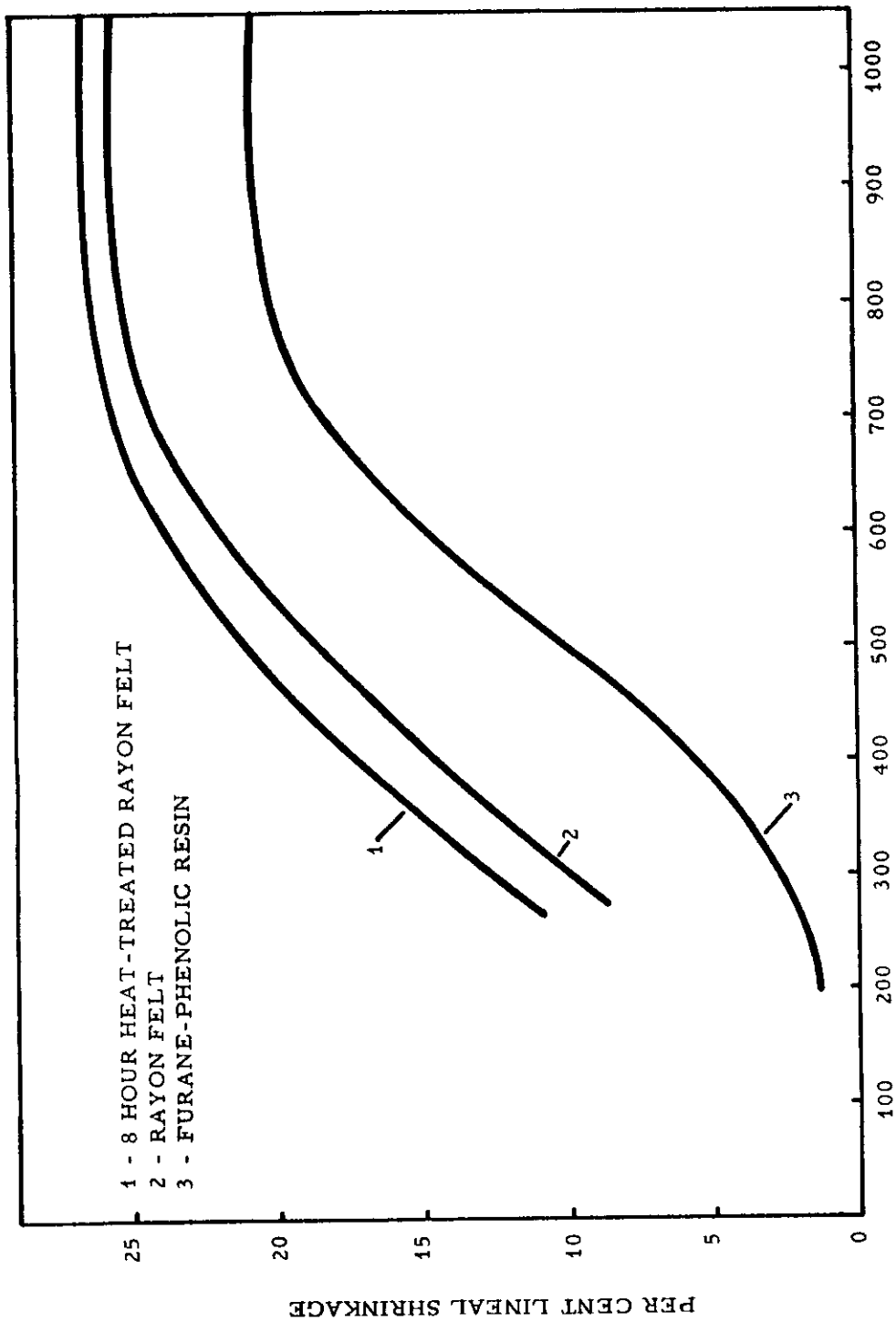

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Figure 31. Lineal Shrinkages of Binders and Filler versus Heat-Treatment Temperature

5.4.5. Conclusions, Carbonaceous-Felt Composites

Initial characterization of felt structures proved that they were superior in strength to cloth composites and laminates. Extensive studies of cloth composites and laminates resulted in their properties being improved to match those of felt structures. Because the cloth composites were more easily processed, work on felt fillers was curtailed. Conclusions reached in the carbonized-felt investigation, however, may be of value in future work and are included in this report.

1. The maximum coking value was reached when the felt was heat treated for 6 to 10 hours at 220°C.

2. Thermal history of carbon felt should be closely monitored to achieve uniform shrinkage in the felt structure. Electrical resistance measurement offered a good quality-control tool for this purpose.

3. Maximum flexural strengths were obtained from laminates containing fillers processed to 600°C. Higher strengths were possible at lower heat-treatment temperatures, but processing the fabricated article became more difficult.

6. EFFECT OF IMPREGNATION ON THE PROPERTIES OF FIBROUS COMPOSITES

As in the fabrication of conventional graphite grades, impregnation with pitch (or with a thermosetting liquid of high coking value), followed by a carbonizing heat treatment, will increase both the strength and bulk density of fibrous composites. In the case of fibrous composites, a relatively small increase in density is accompanied by a remarkable increase in strength. By way of comparison, impregnation of a conventional commercial graphite increases the density approximately 6 per cent and the strength about 30 per cent. Impregnation of a macerated-fibrous composite, on the other hand, results in a density increase of approximately 15 per cent and the strength is increased by a factor of 2 or 3.

The procedures used to impregnate fibrous composites are the same as those employed for impregnating conventional graphite grades. The carbon or graphite body is placed under vacuum in an autoclave. The impregnant is then drawn into the autoclave until the article to be impregnated is completely covered, and pressure is applied for the desired length of time. Following this operation, the autoclave is drained, the impregnated article is removed and baked or graphitized. Multiple impregnations may be employed to increase further the strength and the density of the material; however, the effects produced by impregnation diminish rather rapidly after the initial treatment.

6.1. Impregnation of Macerated-Graphite-Cloth Composites

The effect of impregnating with a furane-resin on the properties of macerated-graphite-cloth composites is summarized in Table 37. Both the 800°C baked (PT-0113) and 2800°C graphitized (PT-0114) composites were impregnated, rebaked to 750°C and measured for physical properties. After impregnation these grades were designated as PT-0153 and PT-0154, respectively. Grade PT-0113 after two impregnations was designated as PT-0146.

The composites used in the impregnation trials reported in Table 37 were made before the forming pressure was increased from 750 lbs/in^2 to 1535 lbs/in^2, (see Section 2.1.2.1), which accounts for the low strength of the base material. The results of a more recent impregnation study of these grades, made at a forming pressure of 1535 lbs/in^2, are shown in Table 38.

Table 37. Effect of Impregnation and Rebaking to 750°C on Properties* of Macerated-Fibrous Composites

Base Grade	PT-0113			PT-0114	
Grade	PT-0113	PT-0153	PT-0146	PT-0114	PT-0154
Number of Impregnations	0	1	2	0	1
Bulk Density, g/cc	1.07	1.24	1.40	0.93	1.21
Specific Resistance, 10^{-4} ohm-cm	170	82	73.40	42.00	33.00
Flexural Strength, lbs/in^2	1,000	3,000	3,350	1,320	3,000
Young's Modulus, 10^6 lbs/in^2	1.40	1.80	2.82	0.94	1.38
Specific Strength, inches	26,000	67,000	66,000	39,000	69,000

* All properties are measured with the grain
N = 5 for all properties

Table 38. Effect of Impregnation and Rebaking to 750°C on Properties of Macerated-Cloth Composites

Grade	PT-0113	PT-0153	PT-0114	PT-0154
Bulk Density, g/cc	1.18	1.32	1.15	1.38
Flexural Strength, lbs/in^2				
w.g.	2060	4230	2450	5570
a.g.	440	590	730	1800
Compressive Strength, lbs/in^2				
w.g.	2970	9320	2040	6950
a.g.	3700	10,200	2520	9570
Young's Modulus, 10^6 lbs/in^2				
w.g.	1.23	2.07	0.89	1.70
a.g.	0.43	0.95	0.28	0.98
Specific Resistance, 10^{-4} ohm-cm				
w.g.	119.8	89.4	31.0	27.5
a.g.	288.6	170.8	62.0	50.5
C.T.E., 25 to 100°C 10^{-6}/°C				
w.g.	1.32	2.10	1.10	2.13
*Specific Strength, inches	48,585	89,053	59,180	112,000

n = 44-67 Bulk density
n = 15-31 Young's modulus
n = 6 Compressive strength
n = 8-13 Flexural strength
n = 17-35 Specific resistivity
n = 3 C.T.E.
* Ratio of flexural strength in lbs/in^2 to bulk density in lbs/in^3

6.2. Impregnation of Graphite-Cloth Laminates

Impregnation also produced an impressive effect on laminated-graphite-cloth composites as it did on macerated-cloth structures. Table 39 summarizes the effect of a single furane-resin impregnation and rebake on the properties of grade PT-0111 which becomes grade PT-0156 after impregnation. The data in Table 39 again illustrate the improvement in strength obtained by impregnation.

Table 39. Effect of Impregnation and Rebaking to 750°C on Properties* of PT-0111 Graphite-Cloth Laminates

Base Grade	PT-0111	
Grade	Before PT-0111	After PT-0156
Bulk Density, g/cc	1.16	1.30
Flexural Strength, lbs/in^2	3200	7250
Young's Modulus, 10^6 lbs/in^2	1.05	1.50
Specific Strength, inches	76,000	154,000

* All properties are measured with the grain

6.3. Impregnation of Carbon-Cloth Laminates

Impregnation of carbon-cloth laminates (PT-0099) with a furane resin did not result in as much of an increase in strength as produced by the impregnation of graphite-cloth laminates (PT-0111). This is evidenced by a comparison of the properties for impregnated-carbon-cloth laminates in Table 40.

Table 40. Effect of Impregnation and Rebaking to 750°C on Properties of PT-0099 Carbon-Cloth Laminates

Base Grade	PT-0099	
Grade	Before PT-0099	After PT-0163
Bulk Density, g/cc	1.06	1.25
Flexural Strength, lbs/in^2	3200	4100
Young's Modulus, 10^6 lbs/in^2	1.14	1.80
Specific Strength, inches	83,000	91,100

When the carbon cloth was formed into a laminate, baked, and graphitized, a nearly continuous phase of coked resin existed throughout the structure. This laminate, when tested in flexure, fractured as a brittle material with all layers contributing to the strength of the specimen (see Figure 20). Graphite cloth retained the resin on the surface of the fibers and in the interstices between the fibers. When the graphite cloth was formed into a laminate, baked, and graphitized, the coked resin was located between the layers. This graphite-cloth laminate when tested in flexure, fractured by delamination (see Figure 20). When PT-0099 was impregnated and rebaked, the impregnant was required to increase the strength of the cloth filler before the carbon-cloth laminate showed a strength improvement. With graphite-cloth laminates, impregnation reinforced the bonds between the layers. Since the impregnant was more effective at increasing the inter-lamina bond strength of PT-0111 than in strengthening the filler of PT-0099, impregnated-graphite-cloth laminates were much stronger than impregnated-carbon-cloth laminates.

6.4. Impregnation of Carbon-Felt Laminates

Laminates of carbon felt (PT-0033) also have been impregnated with a furane resin, and rebaked. The effect of impregnation of this material is shown in Table 41.

Table 41. Effect of Impregnation and Rebaking to 750°C on the Properties of Felt Laminates

Base Grade Grade	PT-0033	PT-0155
Bulk Density, g/cc	0.98	1.23
Flexural Strength, lbs/in^2	2450	4100
Young's Modulus, 10^6 lbs/in^2	1.03	1.80
Specific Strength, inches	69,360	91,000

Although the strength of the PT-0033 material is lower than that usually obtained, the improvement due to impregnation and rebaking is evident.

7. APPLICATIONS AND TEST RESULTS OF FIBROUS COMPOSITES

Fibrous carbon and graphite materials display high specific strength, low thermal conductivity, and excellent thermal shock resistance; therefore, structures produced from these materials show potential for high temperature aerospace applications. During this program, 180 samples were provided to 13 systems contractors for evaluation of properties and/or environmental testing of hardware components. This involved developing 12 different fabrication techniques, the most important or unusual of which have been described previously in this report. Complete test results for these samples have not been received so a detailed account of the performance of these materials as hardware components cannot be presented. A brief discussion, however, of specific applications and available test data will demonstrate the versatility and potentiality of these materials.

7.1. Applications

The examples cited in this section will illustrate typical applications for macerated-fibrous composites and laminated-fibrous composites, principally as components of rocket motors. From a materials standpoint, both the cured and the temperature-stabilized forms should find numerous applications. Resin-bonded materials should excel in areas where conventional refractories melt, provided a certain amount of outgassing can be tolerated. The more demanding areas requiring temperature-stabilized materials could be served with fully-carbonized or graphitized-fibrous-composites which possess properties not found in conventional graphites or other refractories.

7.1.1. Entrance Caps

Several of the fibrous materials have been considered for application in various entrance cap designs. Figure 32 shows an entrance cap (machined from felt laminate, PT-0033) which was designed for use with a solid propellant rocket test motor. The laminate was cured, baked and graphitized prior to machining to the final shape.

Entrance caps of a different design were machined from grades PT-0113 and PT-0091. Figure 33 is an illustration of an entrance cap made from a macerated-graphite-cloth composite (grade PT-0113). This composite was cured and baked to carbonize the resin prior to final machining.

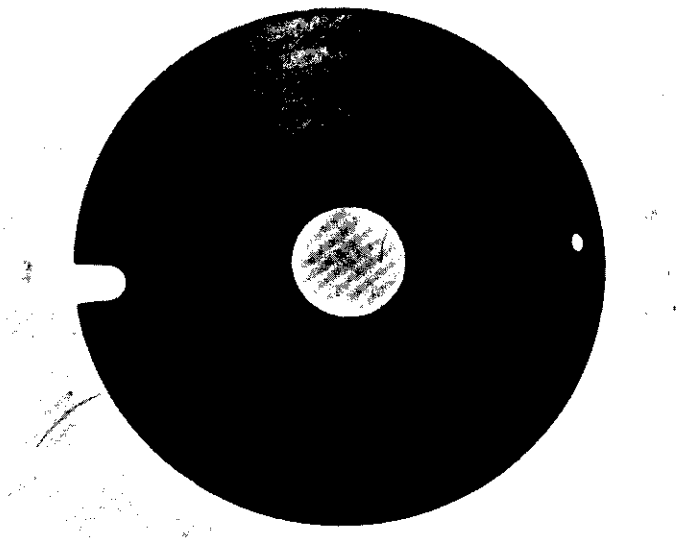


Figure 32. Entrance Cap for Solid Propellant Rocket Test Motor, Grade PT-0033 Felt Laminate

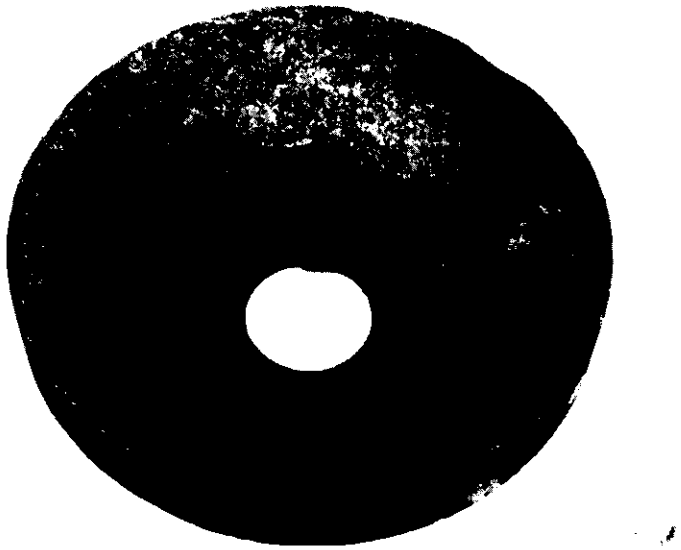
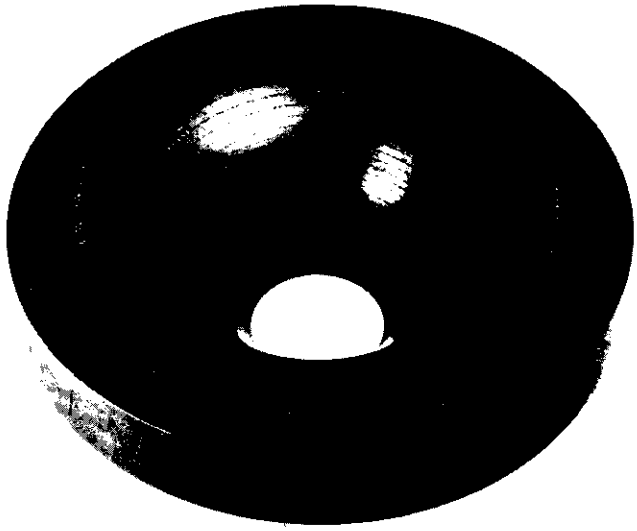


Figure 33. Entrance Cap of Grade PT-0113

An entrance cap of the same design was also machined from grade PT-0091 (Figure 34) which was fabricated from felt reinforced with a cloth insert (see Section 5.1.3). Although this material has unusually high strengths in the cured form, the dissimilar shrinkage rates of the cloth and felt make baking and graphitizing extremely difficult.



FELT LAMINATE - CLOTH
REINFORCED ENTRANCE CAP

Figure 34. Photograph of PT-0091 (Inserted Felt) Entrance Cap

A method for fabricating entrance caps of the above designs by forming them directly to shape would be desirable from two considerations. First, the process would be economical from the standpoint of material requirement and machining. Second, the erosion resistance of the material should be improved because the process would orient the fibers parallel to the working surface. Tooling for fabricating entrance caps to shape was designed and is shown in Figure 35.

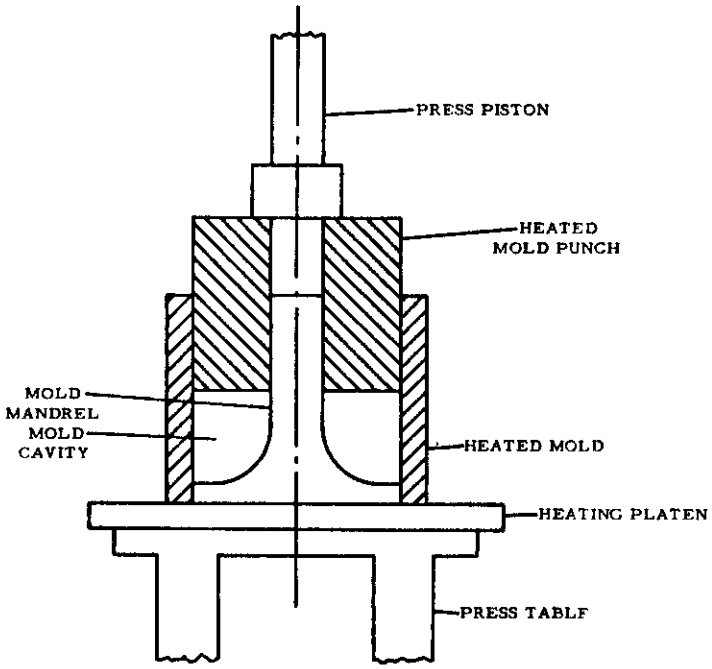


Figure 35. Mold for Forming Entrance Caps to Shape

Forming an entrance cap to shape from carbon felts is described as an example of the operation of this tooling. Annular pieces of resin-impregnated-carbon felt were placed in the mold cavity, and mechanical pressure was applied through the mold punch. The molding pressure was maintained until the piece was cured by heat supplied from the punch, mold and platen. After the cured entrance cap was removed from the mold, the surface opposite the contour was machined to final dimensions. A cross section of a carbon-felt (PT-0031) entrance cap, which was formed to shape is shown in Figure 36. It will be noticed that the process oriented the felt layers so that they followed the contour of the working surface.

Figure 36. Sectioned View of PT-0031 Entrance Cap Formed to Shape

7.1.2. Exit Cones

Fibrous composites have been considered for use as exit cone liners. Figure 37 is an illustration of an exit cone liner fabricated from grade PT-0154, an impregnated composite of macerated-graphite cloth. For thin wall sections, such as exit cone liners, these fibrous materials can be fabricated to shape, and nearly to final dimensions, thus orienting the grain of the composite parallel to the working surface. Scale up of this method to produce large exit cone liners does not appear difficult.

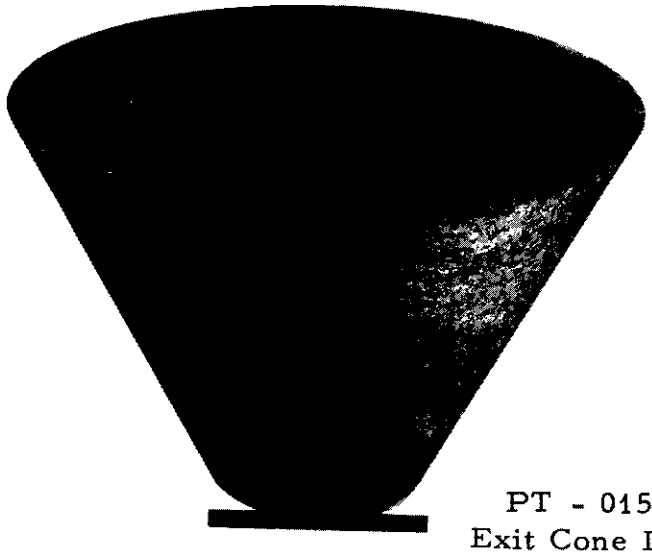


Figure 37. Exit Cone Liner of Grade PT-0154 Graphite

The fibrous graphites can be used in combination with other materials for exit cone applications. An assembly employing a combination of PT-0113 fibrous graphite with grade ZT-4001 graphite is shown in Figure 38. Grade ZT-4001 is a high density, recrystallized graphite, the development of which has been described in WADD Technical Report 61-72, Volume VII. The excellent erosion resistance of

of the ZT graphite and the thermal insulating properties of PT-0113 material presented advantages in this exit cone design. For this

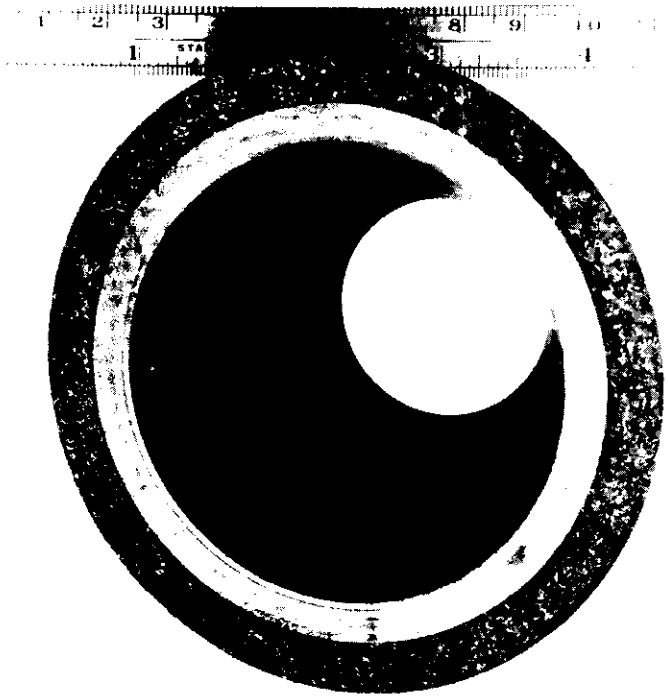


Figure 38. Grade ZT-4001 Graphite Exit Cone Liner with Grade PT-0113 Backup

configuration, the PT-0113 material was fabricated around the ZT-4001 blank, the entire assembly was baked and machined to final dimensions. A strong bond existed between the two materials at the interface.

Figure 39 shows an example of Grade PT-0112 used in combination with a vitreous material, in this case, silica fibers. In this design the PT-0112 was formed to shape and the silica fiber mixture was bonded in a conical shape around the PT material. In operation as an exit cone, the PT-0112 forms the ablative working surface which is insulated by the silica.

Exit cone shapes have also been produced from laminated-carbon cloth as shown in Figure 40. The laminated-exit-cone liner in this figure is shown before impregnation (grade PT-0111), and after impregnation and rebake (grade PT-0156). The exit cone was fabricated with the cloth layers parallel to the working surface. Liners of this type offer potential in applications requiring higher strengths than can

be obtained with grade PT-0154.

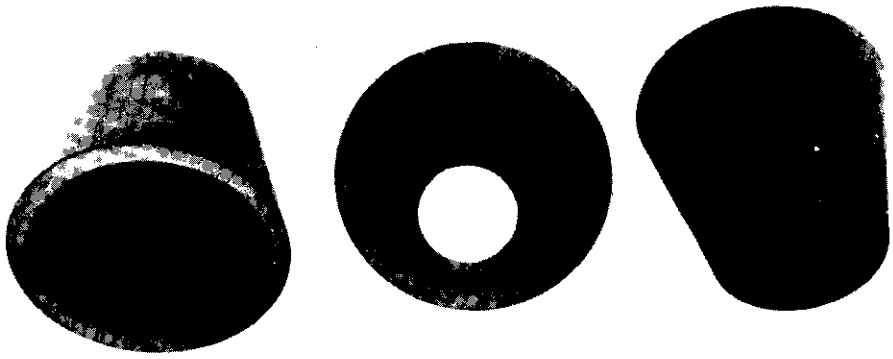


Figure 39. Exit Cone Made from Grade PT-0112 Macerated-Cloth Composite Backed Up with Molded Silica Fibers

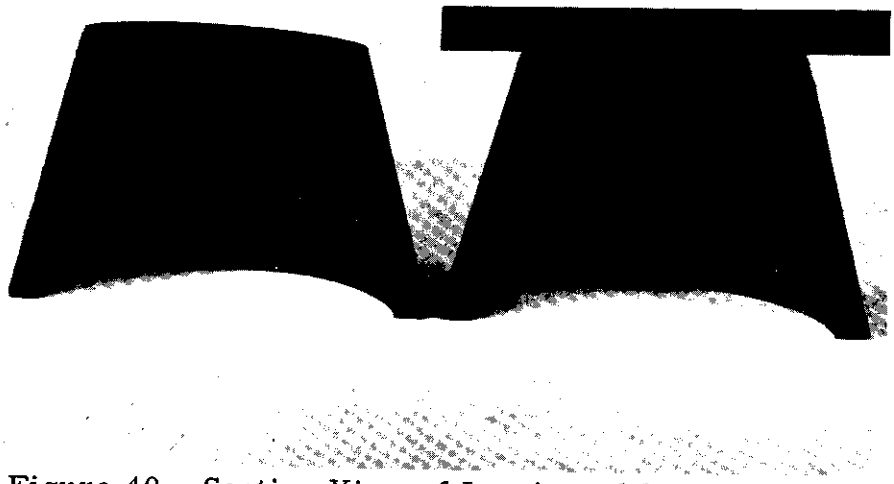


Figure 40. Section View of Laminated Exit Cone Before and After Impregnation

7.1.3. Backup Materials for Rocket Motor Nozzle Inserts

Temperature-stabilized-fibrous composites, in rocket nozzle applications where erosion is a critical factor, have been limited to backup or insulation uses because of their relatively poor erosion resistance as compared to high density graphite and tungsten.

Tungsten nozzles exhibit relatively good erosion resistance but their weight is a disadvantage. Fabrication of a tungsten nozzle backed up with a carbonized-fibrous composite would permit utilization of the erosion resistance of tungsten, and the light-weight and desirable high temperature thermal properties of fibrous materials. Figure 41 shows a tungsten-tantalum insert before and after being backed up with grade PT-0113. A similar application with a thin-wall, rolled, tungsten liner is shown in Figures 42 and 43. In Figure 43 a section of the fibrous backup material has been cut away to show the degree of adhesion to the tungsten liner.

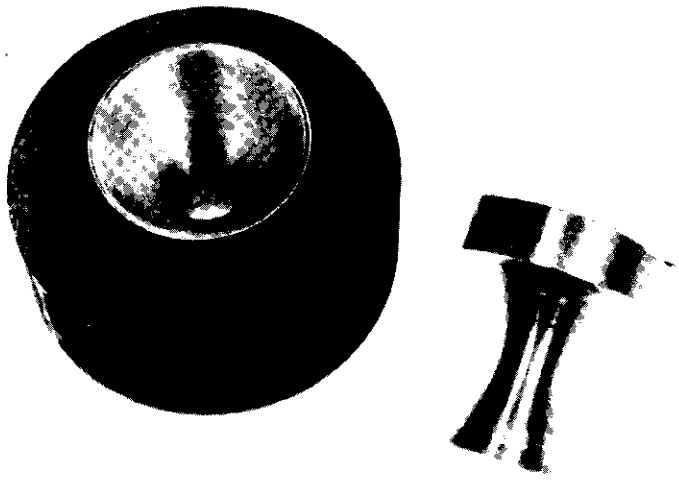


Figure 41. Tungsten-Tantalum Insert Before and After Fabrication of Grade PT-0113 Backup

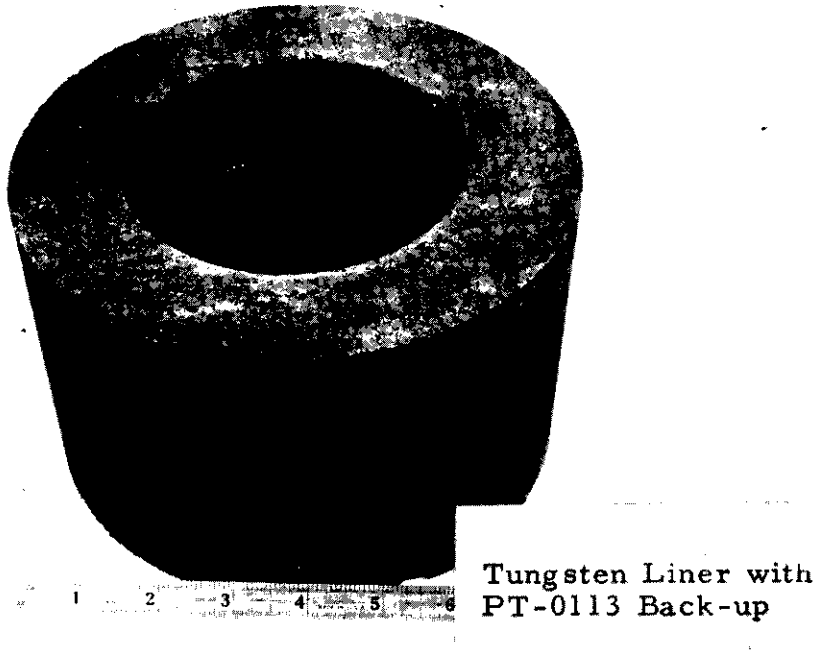


Figure 42. Tungsten Liner with Grade PT-0113 Backup

Figure 43. Section View of Tungsten Liner with Grade PT-0113 Backup

A simple yet unusual method of forming fibrous backup materials onto intricate-shaped-graphite nozzle inserts was developed to overcome the limitations of conventional and isostatic forming. This forming method, referred to as slip-band forming, was based on the principle that fibers should be applied around the insert by a force always in the direction toward, and perpendicular to, the axis of the nozzle insert. In this way the grain of the fibrous composite would tend to be oriented parallel to the insert axis and the forming pressure would be uniform over the length of the insert. A slip-band assembly, shown in Figure 44, was used to accomplish the desired effect. The slip band consisted of a sheet metal strip with interlacing, slotted ends as shown in the top view in Figure 44. When the ends were attached to a specially adapted hydraulic cylinder (lower right of Figure 47) and pressure applied, the band formed a contracting cylindrical shell which exerted the molding pressure in the desired direction around the nozzle insert as shown in the lower left of Figure 44.

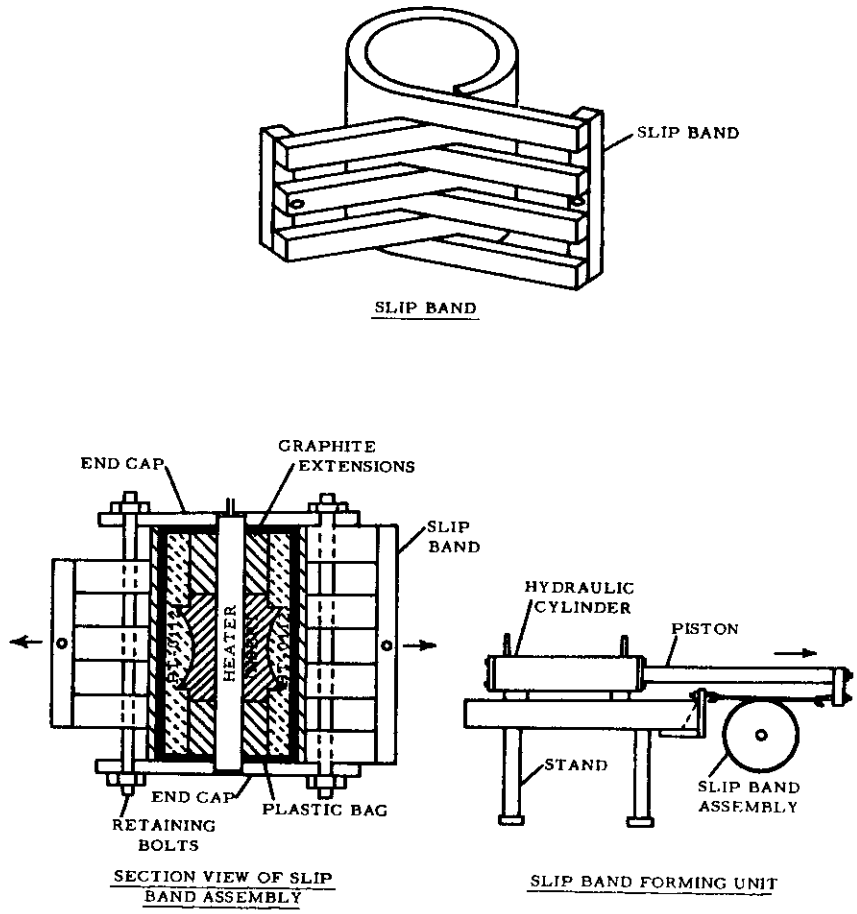


Figure 44. Schematic of Tooling for Slip-Band Forming

The photograph shown in Figure 45 compares a fibrous-graphite backup fabricated by the slip-band method and one formed by isostatic methods. From this photograph, it appears that a much more tenacious bond was obtained with the slip-band method. Of interest, also is the fiber alignment shown in Figure 45. Slip-band forming forced the fibers to conform to the contour of the insert which was conducive to shrinking the fibers tightly around the insert during baking, and eliminating the separation at the interface. The random fiber orientation obtained with isostatic forming allowed the fibers to shrink away from the insert during baking.

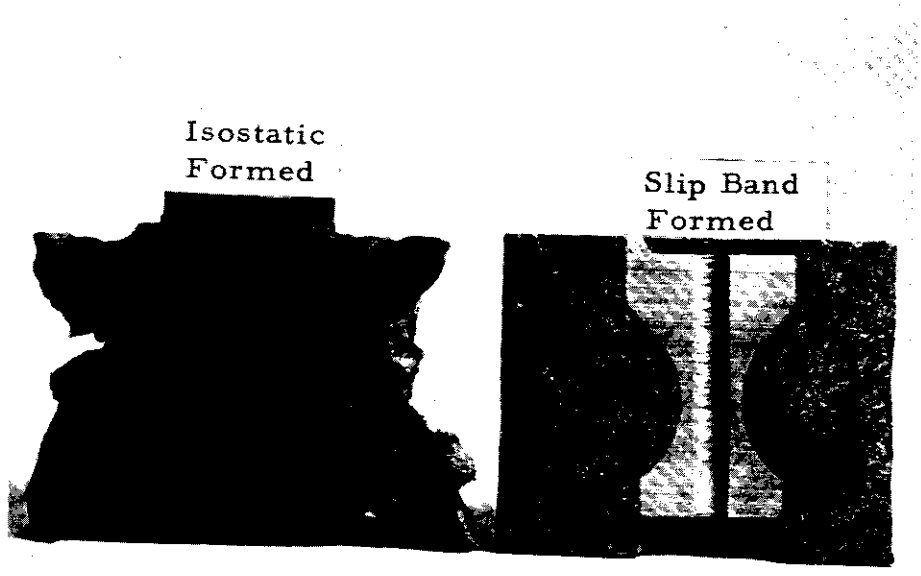
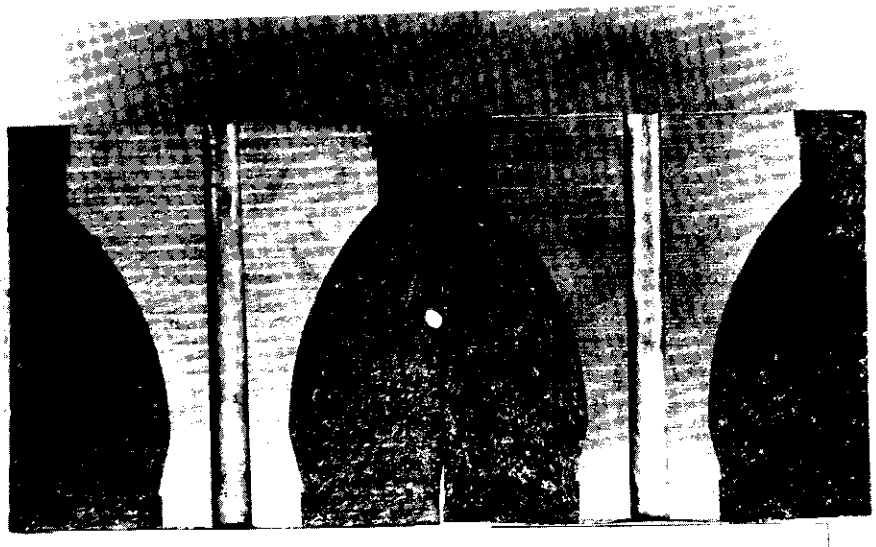


Figure 45. Photograph of Cross Section of Backup Fabricated by Isostatic and Slip-Band Methods

Figure 46 shows a fibrous backup fabricated by slip-band forming around a rocket nozzle insert of a different configuration. The excellent bond between the two materials, which is obtained by this forming method, again is evident in both the cured and baked states.



Slip Band Formed
Cured

Slip Band Formed
Baked

Figure 46. Slip-Band-Formed Backup in the Cured and Baked States

7.1.4. Nose Cones

The fibrous composites have been considered, in combination with other graphites, for use in nose cone applications. A design for such a nose cone is shown in Figure 47 and consists of a conical shape, machined from grade PT-0113, cemented inside an ATJ graphite shell. The machined PT-0113, before it was cemented into the ATJ shell is shown in Figure 48. The cement used for bonding was a furane-phenolic resin, the same as used for binder in the PT-0113, and was fully carbonized after the pieces were joined.

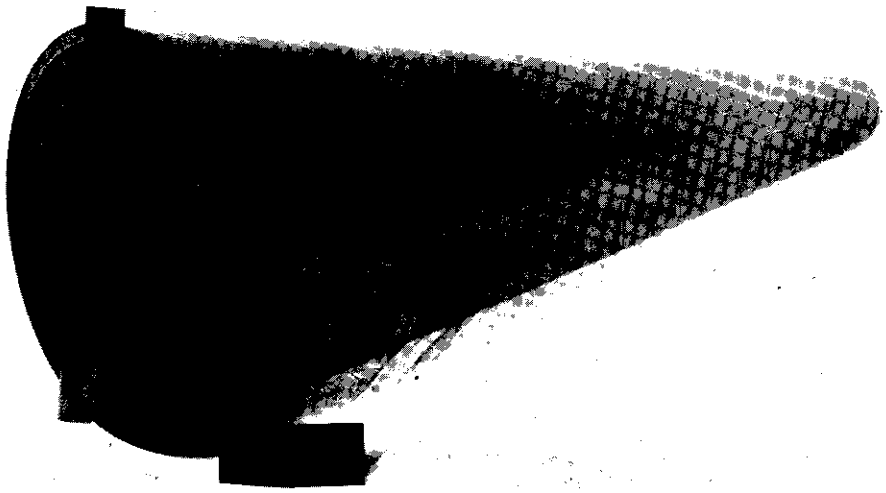


Figure 47. Nose Cone Combining Grade ATJ Graphite and PT-0113

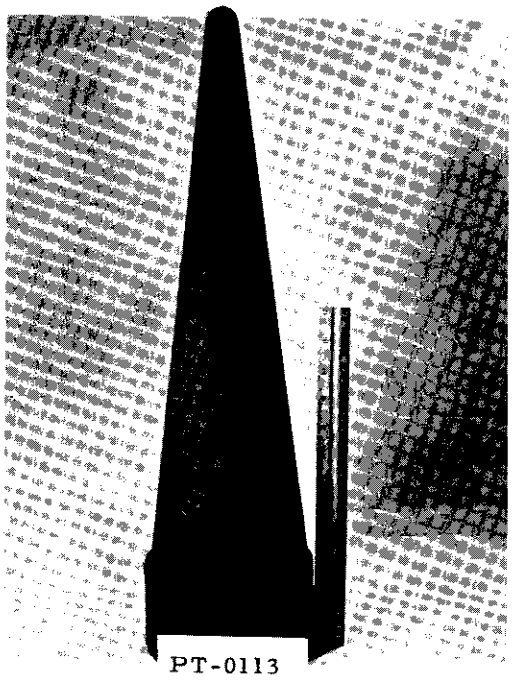


Figure 48. Nose Cone Insert Grade PT-0113

Another possibility for nose cone applications is fibrous composites coated with pyrolytically deposited carbon. Graphite-cloth composites which have been thermally stabilized are excellent substrates for pyrolytic-carbon coatings because their fibrous nature and low elastic modulus allow them to expand and contract with the coating. Although the thermal expansions of the coating and substrate are dissimilar, thermal cycling can be accomplished without failure. The porous nature of the fibrous composite also facilitates formation of a tenacious bond between the coating and substrate. Penetration of the coating is restricted, however, to the surface of the substrate, thereby preventing gross property changes in the substrate.

Grades PT-0113 and PT-0114 were used as substrates for coating with pyrolytic carbon. Figure 49 shows a small test cone before and after application of the pyrolytic coating. Nozzles of grade PT-0114 also were coated internally with a thin shell of pyrolytic graphite. Such nozzles have been annealed to 2000-2500°C in a protective atmosphere with no adverse effects.

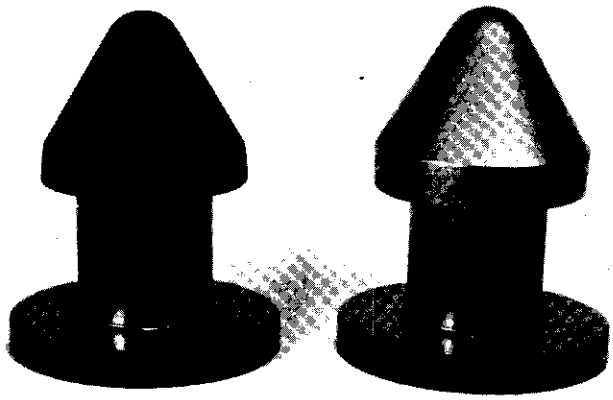


Figure 49. Grade PT-0114 Test Nose Cones Before and After Pyrolytic Coating

7.1.5. Miscellaneous Applications

The laminated-graphite-cloth structures (PT-0111) shown in Figure 50 are a tubular section and a flat plate intended for use as a susceptor and cover assembly for an induction-heating application. Because of their improved thermal shock resistance and mechanical toughness, these materials are ideal for such applications.

Graphite-cloth laminates can be fabricated into large-diameter, thin-wall sections and, therefore, can be used to replace bulk graphites for retainers and heat shields in high temperature furnaces.

Figure 50. Grade PT-0111 Susceptor and Cover

The PT-0110 cylinders shown in Figure 51 (20- to 39-inch diameter) were employed as retainers for carbon-felt insulation as illustrated by a similar arrangement shown in Figure 52.

Figure 51. Cylinders Made from Grade PT-0110 Cloth Laminate

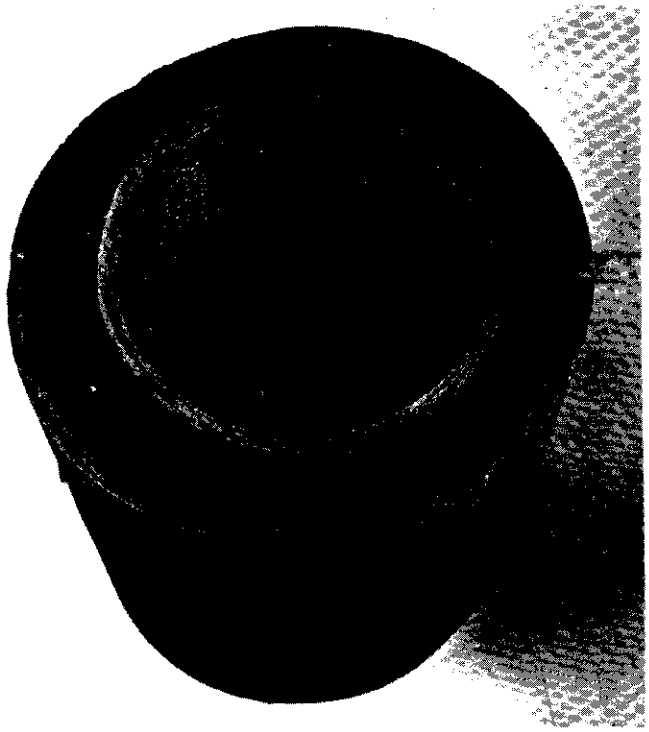


Figure 52. Thermal Shields Made from Grade PT-0110 Shells and Carbon Felt

7.2. Test Results of Fibrous Composites as Missile Components

Evaluation of entrance caps, exit cones, and blast tubes is usually qualitative rather than quantitative. In many instances, the fibrous materials were designed as thermal insulators which must withstand thermal shock rather than erosion. In actual firings, these properties are difficult to evaluate numerically. For example, char depth is used as an index to evaluate the performance of resin-bonded thermal insulators. Since most of the fibrous composites reported herein were temperature stabilized, they show no char depth and this criterion is nonconclusive. The performance of the fibrous materials as entrance caps, exit cones, and blast tubes was based primarily on post-firing-visual inspection.

ZT graphites show very low erosion rates when fired in solid propellant rocket motors but, because of their high density and high degree of anisotropy, they are subject to thermal-stress cracking if the temperature gradient through the nozzle wall is too great. The possibility of thermal-stress cracking can be reduced by using the graphite in a thin-walled section, thereby reducing the thermal gradient. Figure 53 shows a rocket nozzle assembly fabricated with a ZT-4001 graphite insert backed up with PT-0113 fibrous material. In this way, the possibility of thermal-stress failure was reduced without sacrificing the low-erosion characteristics of the ZT graphite. The nozzle was test fired in a 6-inch solid propellant rocket motor and, although the erosion rate was slightly higher than normal because of a higher insert throat temperature of the insert throat, the ZT graphite was not cracked by thermal stresses.

Figure 53. Grades PT-0113 and ZT-4001 Nozzle Assembly

Figure 54 is a photograph of the fired nozzle. After firing, the ZT graphite was not cracked and the bond between the graphite and fibrous composite was still intact.

Figure 54. Post-Firing Section View of Grade PT-0113 Composite and Grade ZT-4001 Graphite

Evaluation of several fibrous grades under simulated blast tube conditions was completed in the subscale rocket motor. This study consisted of mounting 8 test samples in an octagonal configuration in the exhaust stream of the rocket motor. Although the test was not severe from an erosion standpoint, it did give a good thermal shock test under flow conditions. Examination of the fiberglass-blast-tube holder after firing indicated the thermal shielding provided by each sample. Two macerated-graphite-cloth composites (thermally stabilized) were studied, and grade PT-0113 (baked) provided superior thermal protection. Neither grade PT-0113 (baked nor grade PT-0114 (graphitized) showed adverse effects due to thermal shock. A sample of grade PT-0112 (cured) exfoliated because of the rapid evolution of

gases at the high temperatures. Sectional views of these three samples are shown in Figure 55.

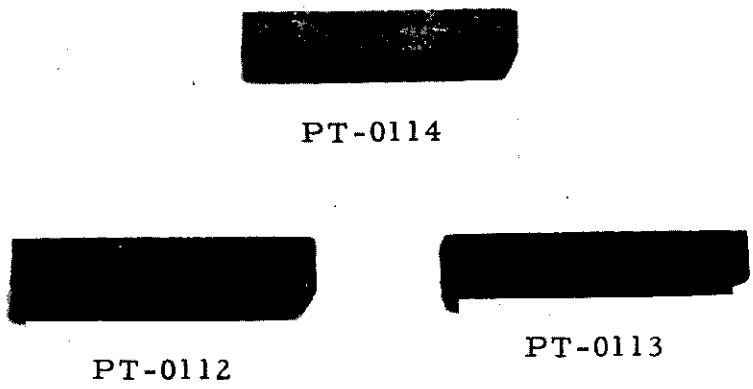


Figure 55. Post-Firing Photograph of Macerated-Graphite-Cloth Blast Tube Samples

A similar evaluation was conducted on the laminated-graphite-cloth structures. Figure 56 is a photograph of cross sections of grades PT-0109 (cured), PT-0110 (baked), PT-0111 (graphitized), and PT-0156 (impregnated and rebaked) after they had been fired under simulated blast tube conditions. Grades PT-0109 and PT-0110 showed evidence of delamination which was attributed to low across-the-grain strengths and to gas evolution during the firing.

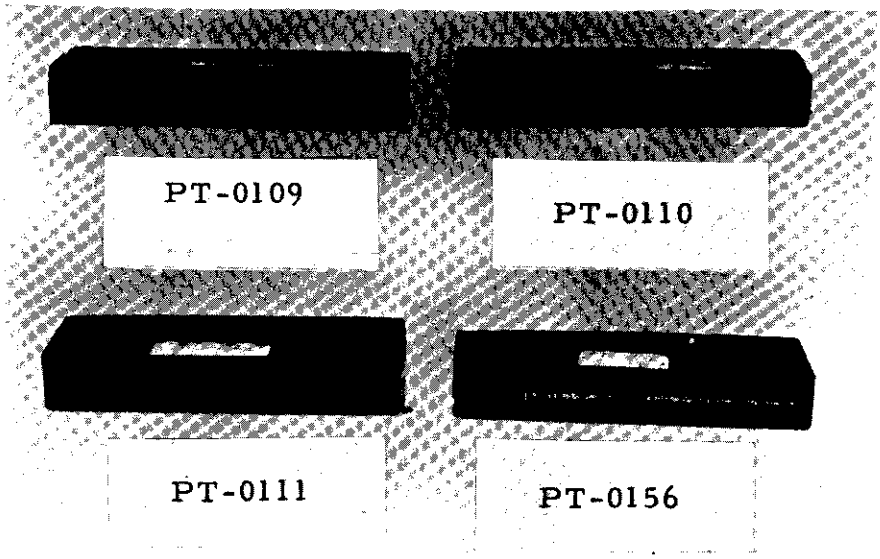


Figure 56. Post-Firing Photograph of Laminated-Graphite-Cloth Blast Tube Samples

The laminated-carbon-felt grades PT-0031 (cured), PT-0032 (baked), and PT-0033 (graphitized) were evaluated under the same blast tube conditions and similar results were obtained. The photograph in Figure 57 shows, again, that the cured sample delaminated during firing because of the evolution of gases from the uncarbonized resin.

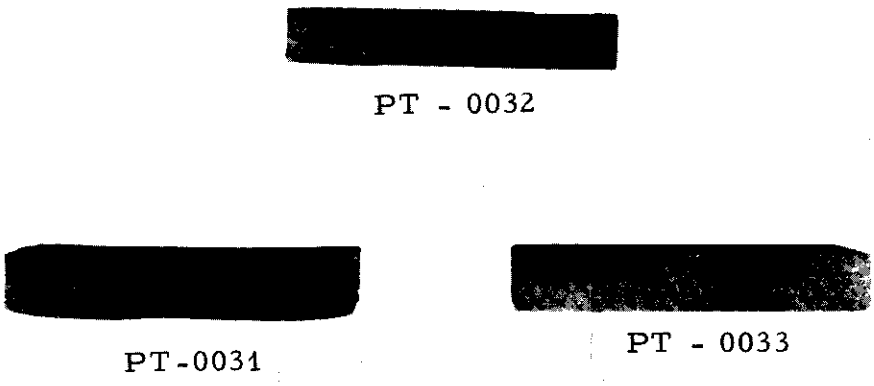


Figure 57. Post-Firing Photograph of Laminated-Carbon-Felt Blast Tube Samples

8. GENERAL CONCLUSIONS

1) Of all the materials investigated, WCA square-weave-graphite cloth is the superior filler material for producing thermally-stable-fibrous composites.

2) WCA graphite-cloth structures, both macerated and laminated, have specific strengths (59,000 to 76,500 inches) comparable to ATJ graphite (64,000 inches).

3) Thermal conductivity of macerated-graphite-cloth composites after graphitization is approximately one-fifth that of ATJ graphite, 12.2 BTU-ft/ft^2 hr°F and 68 BTU-ft/ft^2 hr°F, respectively.

4) Specific strengths of macerated-graphite-cloth composites and graphite-cloth laminates are markedly improved by impregnation with furane resin and rebaking; strengths are 59,000 to 112,000 inches and 76,500 to 154,000 inches, respectively.

5) Fibrous structures show much potential for use in aerospace applications because of their ease of fabricating, their desirable mechanical and thermal properties, and their ease of machining.

APPENDIX I. SUMMARY OF PROCESSING DESCRIPTION OF "PT" GRADES

Table 42. Unimpregnated Grades of Fibrous Composites

Grade	Base Material	Final Temp. of Base Material	Binder	Forming Method	Final Temp. of Product
PT-0109	Graphite Cloth	2800°C	Furane-Phenolic	Laminated	130°C
PT-0110	Graphite Cloth	2800°C	Furane-Phenolic	Laminated	800°C
PT-0111	Graphite Cloth	2800°C	Furane-Phenolic	Laminated	2800°C
PT-0112	Graphite Cloth	2800°C	Furane-Phenolic	Macerated	130°C
PT-0113	Graphite Cloth	2800°C	Furane-Phenolic	Macerated	800°C
PT-0114	Graphite Cloth	2800°C	Furane-Phenolic	Macerated	2800°C
PT-0099	Carbon Cloth	800°C	Furane-Phenolic	Laminated	2800°C
PT-0031	Carbon Felt	800°C	Phenolic	Laminated	130°C
PT-0032	Carbon Felt	800°C	Phenolic	Laminated	800°C
PT-0033	Carbon Felt	800°C	Phenolic	Laminated	2800°C
PT-0091	Inserted-Carbon Felt	800°C	Phenolic	Laminated	130°C

Table 43. Impregnated Grades of Fibrous Composites

Base Grade	Number of Impregnations	Rebaking Temperature	New Grade
PT-0113	1	800°C	PT-0153
PT-0114	1	800°C	PT-0154
PT-0113	2	800°C	PT-0146
PT-0111	1	800°C	PT-0156
PT-0099	1	800°C	PT-0163
PT-0033	1	800°C	PT-0155

10. LIST OF REFERENCES

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