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MASTER

DISCONTINUOUS CARBON-CARBON COMPOSITE FABRICATION

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE   Y-12 PLANT

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UNION CARBIDE CORPORATION
Nuclear Division

OAK RIDGE Y-12 PLANT

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J. L. Cook
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bon Composite Technology Symposium, Albuquerque,
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Oak Ridge, Tennessee

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ABSTRACT

Composites consisting of short fibers in a carbon or graphite matrix were fabricated at the Oak Ridge Y-12 Plant[a] by isotropic casting, flock lay up, spray lay up, and pulp molding. Models of the fiber structures generated by each technique were considered and related to the physical and mechanical properties and processing characteristics. For hollow cylinders, the structural integrity and the rate of densification by repeated liquid resin impregnation, carbonization, and graphitization were influenced by the anisotropic behavior of the fiber structures. Selected properties of the materials resulting from these fabrication techniques were determined.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the United States Atomic Energy Commission.

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CONTENTS

SUMMARY

Four techniques were evaluated for structuring discontinuous carbon-carbon composites. The effects of fiber alignment on the rate of densification by liquid impregnation-carbonization schemes were demonstrated. Anisotropic expansion coefficients were shown to correlate with failures due to anisotropic shrinkage in cylindrical shapes. Preliminary data for electrostatic flocking indicated that the fiber could be aligned normal to the surface of a part or packed randomly around filament windings. Thermal insulating and strength characteristics for low-density, pulp-molded composites were related to processing variables.

Samples of the higher-density composites produced very early in this work have been ablation tested by the Sandia Corporation, and heat of ablation (Q^*) values ranging from 21,000 to 40,000 Btu/lb were obtained in a six-atmosphere, 1,350-Btu/ft^2-sec arc jet test.[1] Use of these four techniques provides the fabricator with a large family of composites with applications ranging from insulators to graphite electrodes.

INTRODUCTION

Technological interest in carbon-carbon[b] composites which possess unique combinations of physical and mechanical characteristics continues to increase. Designers and materials engineers are attracted by such composite properties as a high strength-to-weight ratio, toughness, shock and chemical resistance, and thermal stability. Critical space, weight, and refactory applications exist in industrial, aerospace, and aircraft programs.[2] Without question, an exciting and rewarding future exists for the fabricators who are able to construct carbon-carbon composites which effectively withstand environments too stringent for ordinary monolithic materials.

An area of composite development which has received far too little attention is the fabrication of discontinuous fiber composites. Techniques for forming short, small-diameter ($L/D \geq 100$) fibers into complex shapes, and methods of controlling the fiber-packing density and orientation are needed. Effective incorporation of short fibers into filament-wound structures is required to increase interlaminar strengths. Before extensive use for critical applications, methods must be developed and refined, and a high degree of reproducibility proven.

Discontinuous fiber incorporation techniques selected for evaluation were: isotropic casting, flock lay up, spray lay up, and pulp molding. Program objectives were to demonstrate the applicability of each technique to carbon-carbon composite fabrication, to evaluate the fiber structures developed, and to determine selected properties. Attention was given to developing reproducible procedures, but very little effort was expended to obtain the ultimate properties.

(b) In this report, carbon-carbon composites will be used to include all the composites which may have a carbon or graphite matrix reinforced with carbon fibers.

COMPOSITE FABRICATION

TECHNIQUES AND EVALUATIONS

Fabrication of discontinuous fiber-reinforced plastic composites by lay up, slurry molding, and casting techniques has been described in the literature.[3] Similar methods were applied to carbon-carbon composite fabrication to control the fiber orientations within the carbon or graphite matrix. It was observed that the fiber orientations resulting from the incorporation techniques were primarily responsible for the anisotropic characteristics of the composites. Figure 1 shows models of the fiber arrangements expected from each of the four incorporation methods evaluated: (1) isotropic casting, (2) spray lay up, (3) flock lay up, and (4) pulp molding.

Typically, composite fabrication by any of the techniques consists of the following processes: (1) fiber incorporation or structuring, (2) binder curing and thermal

Flock Lay Up

Pulp Molding
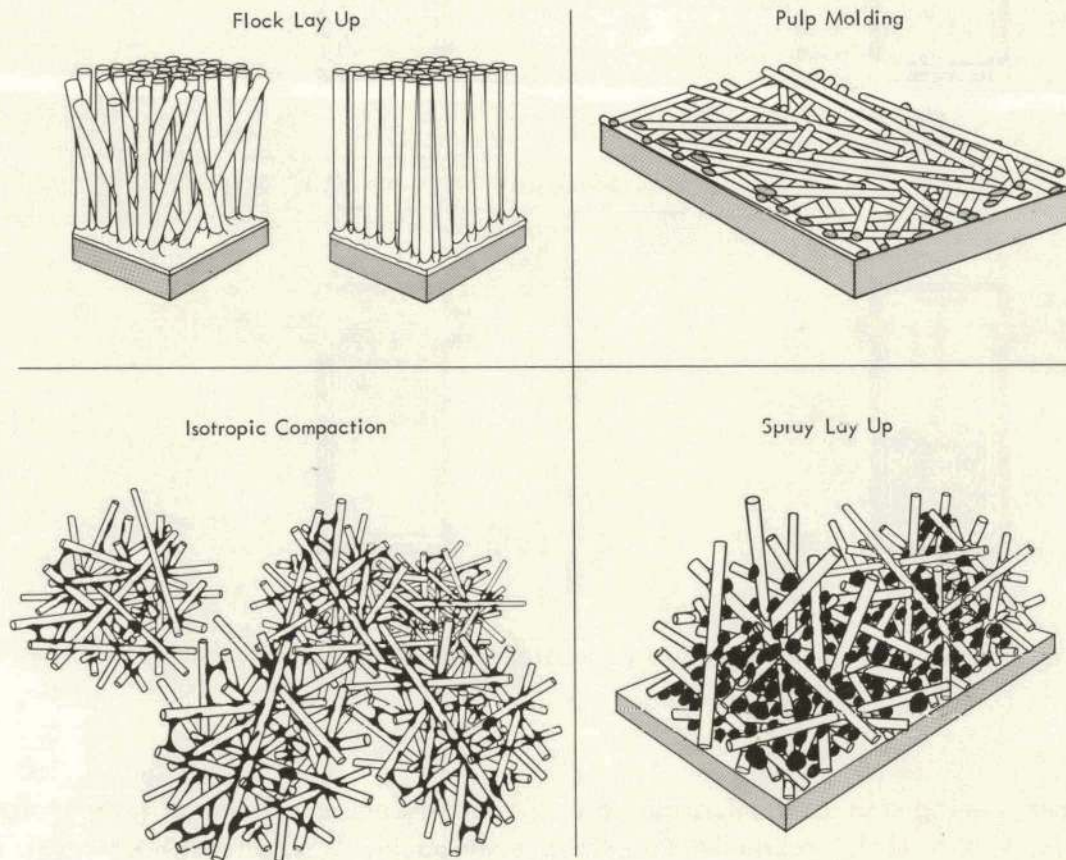
Isotropic Compaction

Spray Lay Up

Figure 1. MODELS OF THE FIBER ARRANGEMENTS EXPECTED FOR FOUR FABRICATION TECHNIQUES.

stabilization, (3) densification (infiltration and/or compaction), and (4) heat treatment for property adjustment.

Densification by repeated impregnation with coal-tar pitch and subsequent carbonization and graphitization was used extensively. Using the technique shown in Figure 2, pitch was infiltrated at a temperature of 200° C and at pressures from 50 to 15,000 psi. Compaction and carbon-vapor deposition were also used to densify certain fibrous structures.

1. Work suspended over impregnant. Vacuum drawn.

Cylinder "Up"
Vacuum
Samples Basket
Impregnant

2. Samples submerged.

3. Vacuum released; pressure applied. Instantaneous impregnation. Pores completely filled.

Pressure In

4. Samples raised and allowed to drain while pressure is released.

Cylinder "Up"
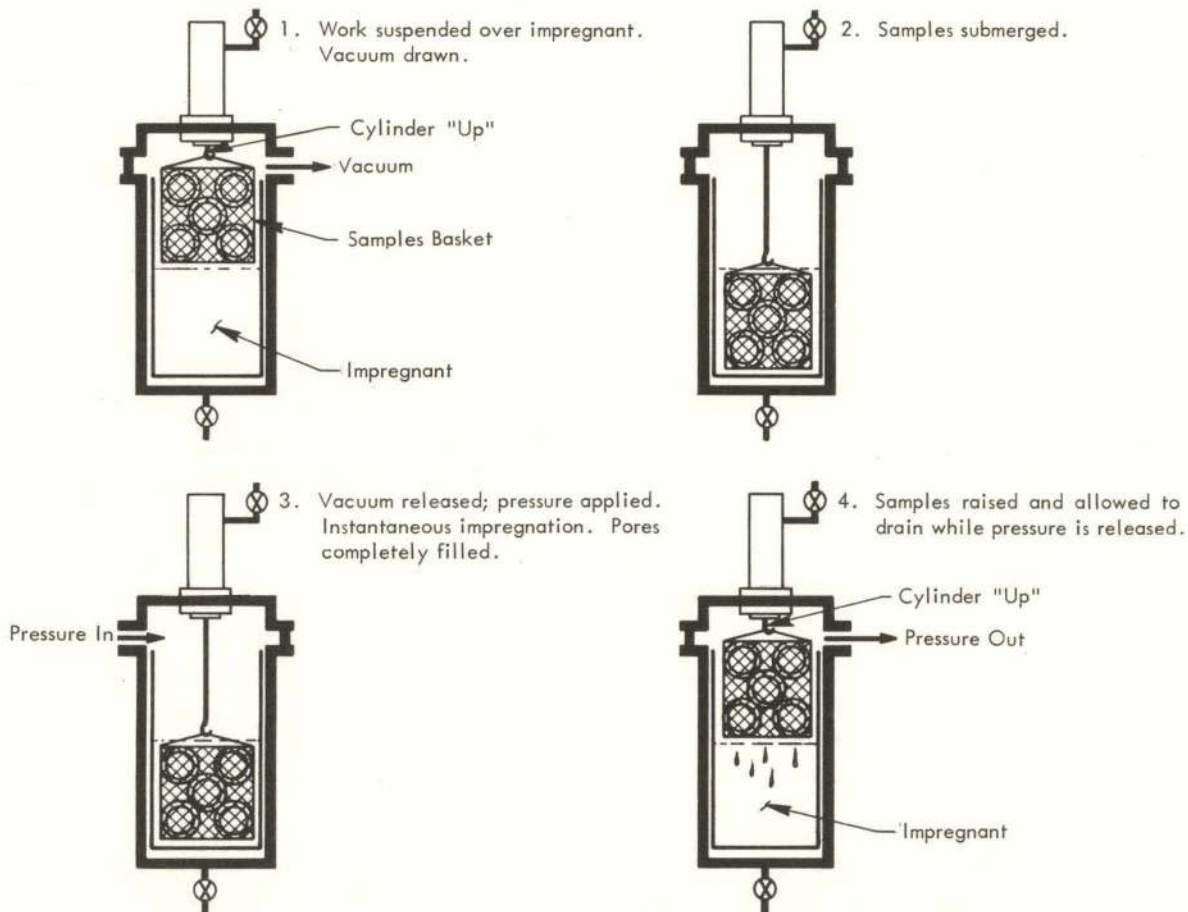Pressure Out
Impregnant

Figure 2. METHOD USED TO VACUUM AND PRESSURE IMPREGNATE CARBON-CARBON COMPOSITES.

Binder curing and carbonization were generally accomplished at temperatures up to 1,000° C by methods described previously.[4] The final heat-treatment temperature depends on the characteristics needed, but most of the composites were heated to between 1,500 and 1,800° C during processing.

Isotropic Casting

Specially prepared carbon fibers (2 μ D x 250 μ L)[5] and particulates of coal-tar pitch[c] were blended together, cast, and warmed under an isostatic pressure of about 15 psi. After cooling with liquid nitrogen, the casting was ground in an impact-type mill[d] to form agglomerates of binder and fiber (about 0.030" D). These agglomerates appeared to have the isotropic fiber arrangement as shown in Figure 3. Using these fiber-binder agglomerates, three types of material were produced which contained fiber/volume fractions of 0.15, 0.30, and 0.37.

High-fiber-content (0.37 vol fraction) solid billets were formed by the warm isostatic pressing and pressure carbonization procedure described previously[4] and shown schematically in Figure 4. Pressure-carbonized and machined billets are shown in Figures 5 and 6. From the initial carbonized and compacted density of 1.2 gms/cc, the billets were densified to 1.75 gms/cc in three pressure impregnation-carbonization cycles. Isotropy of this material was demonstrated by a 1.15/1.00 ratio of the coefficients of thermal expansion (CTE ratio) for two orthogonal directions.

Hollow cylinders of a lower-fiber-content (0.3 vol fraction) material were produced by the same casting techniques, but without mechanical pressure during carbonization. Density of the pressed and carbonized material was about 0.7 gm/cc. Figure 7 shows the microstructure of the isotropic agglomerates; and, at low magnification (Figure 8), some alignment or elongation of the fiber agglomerates in planes normal to the direction of pressing is observed. However, CTE ratios of 1.1 and 1.2/1.0 were obtained for the radial-to-axial and the radial-to-tangential directions, respectively. Thick-wall cylinders (1 to 1.5" T) demonstrated isotropic behavior during processing, and densities were increased from 0.7 to 1.2 gms/cc in one impregnation-carbonization cycle without cracks or delaminations. Pore distributions for two of the isotropic cast materials are indicated by the graph of Figure 9.

The lowest-fiber-content isotropic castings were made by vibrational compaction of the fiber-binder agglomerates and yielded a carbonized density of 0.2 gm/cc. The fiber structure of the castings was similar to that of the agglomerates (Figure 3). Cylinders (2.5" ID with a 0.9" wall thickness) were pitch infiltrated and carbonized at atmospheric pressure from 0.2 to 0.8 gm/cc in one cycle
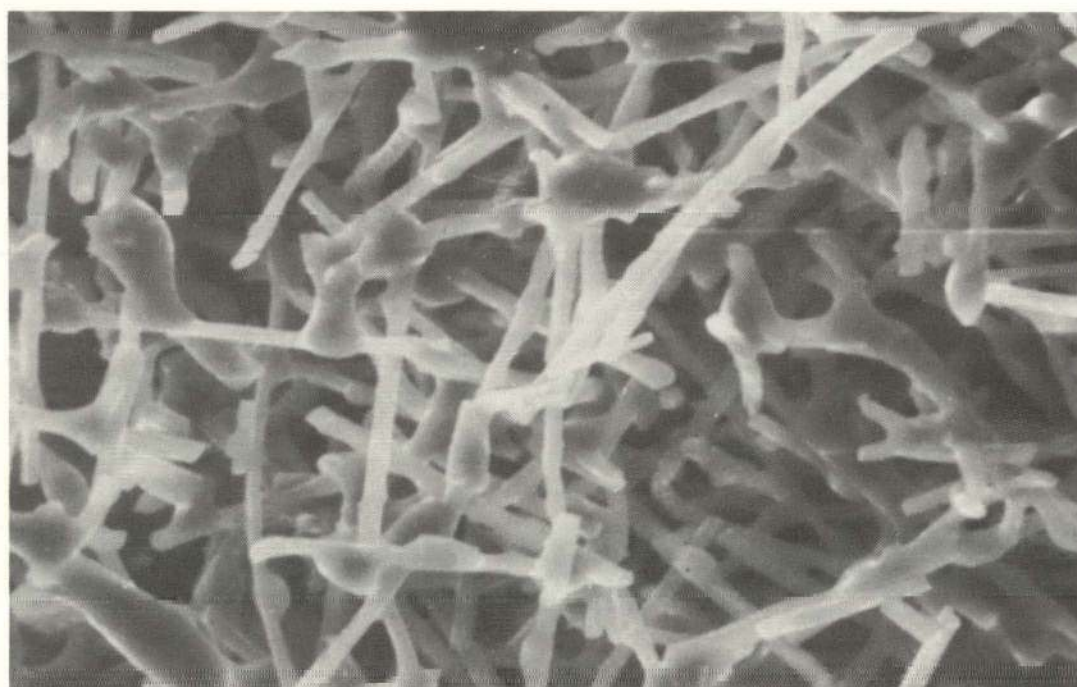

(c) Allied Chemical Corporation's Type CP-227-15V.
(d) Wiley Mill, Standard Model 3.

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(a) 100X

(b) 300X

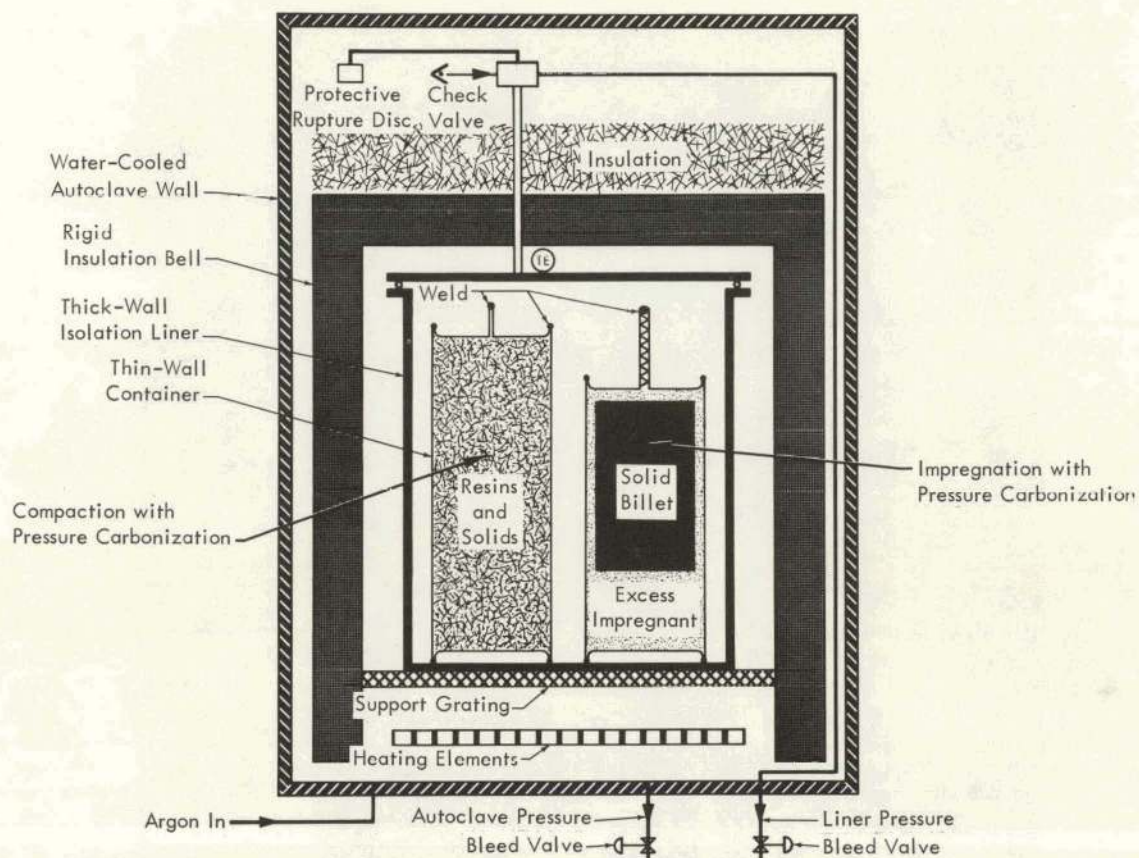Figure 3. SCANNING ELECTRON MICROGRAPHS OF FIBER-BINDER AGGLOMERATES.

Figure 4. TECHNIQUE FOR THE PRESSURE IMPREGNATION-CARBONIZATION CYCLE.

without failure. Further densification to 1.75 gms/cc yielded the structure shown in Figure 10. Although a porosity of 18 percent was observed, 99 percent of the porosity was for pores less than 10 microns. The CTE ratio at a density of 1.0 gm/cc was 1.04/1.00 for the radial-to-axial directions. Rings from the densified cylinders exhibited no residual stress when a radial cut was made.

Spray Lay Up

A previously developed spray-forming procedure[4] which used fibers slurried in a binder diluted with a volatile solvent was improved by the use of continuously evacuated mandrels and nonvolatile solvents. Figures 11 and 12 show a schematic of the lay-up procedure and an exploded view of a cylinder mandrel with a sprayed part. For this vacuum-assisted spraying technique, fibers were slurried in a water-starch solution. The water was removed from the lay up by the vacuum, and the starch[e] was gelatinized and carbonized to form structural bonds. With

_____

(e) Fisher's S-516.

Figure 5. PRESSURE-CARBONIZED BILLET OF AN ISOTROPIC CASTING.

water as the carrier, particles of a secondary binder such as pitch, and fillers such as carbon black, were added to the spray mix. These particles, as shown in Figure 1, help prevent alignment of the fibers in planes parallel to the surface of the mandrel. Porosity measurements on low-density material indicated that the particles also reduced the size and amount of porosity in the fiber structure. A comparison of the improvement in product uniformity over the previous spraying technique is shown by means of a radiograph in Figure 13 and
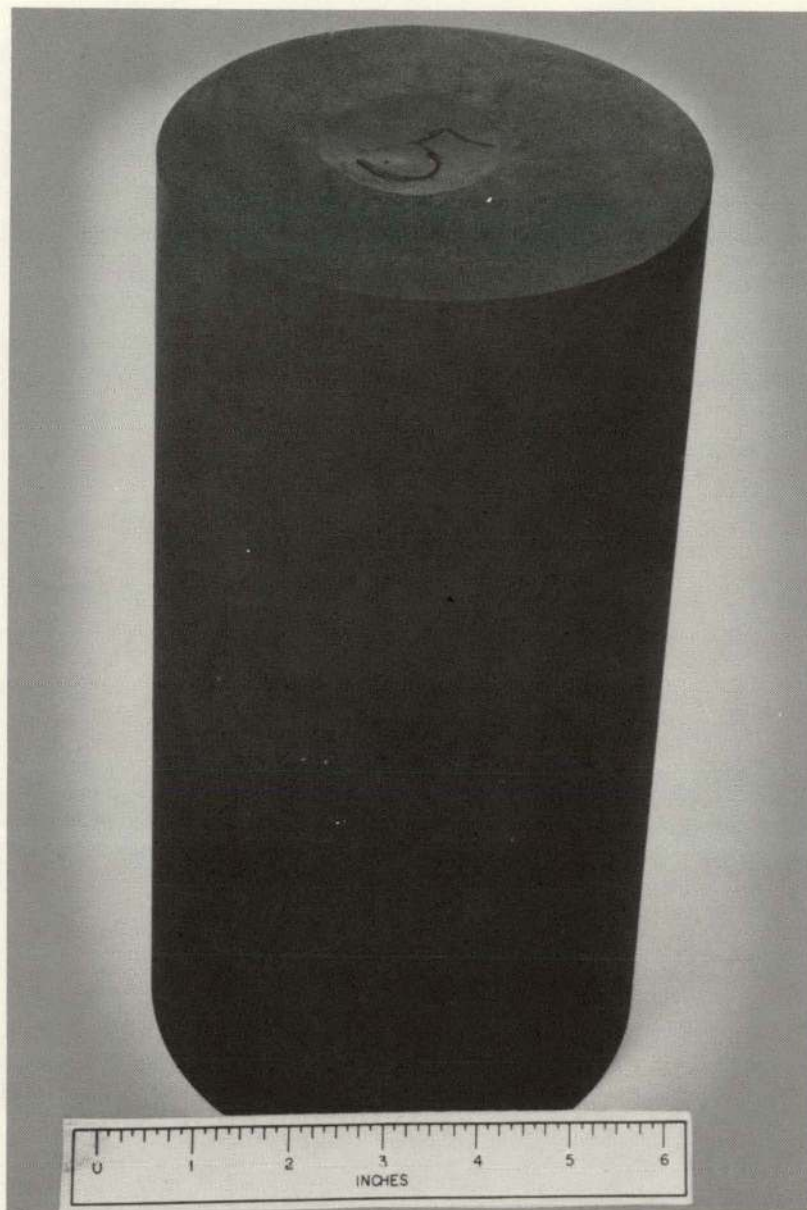
Figure 6. MACHINED BILLET OF AN ISOTROPIC CASTING AT A DENSITY OF
1.15 gms/cc.

pore distributions in Figure 14. Lay-up rates were increased from approximately
0.1 inch/hour for the previous method to 2 inches/hour, and sections up to two
inches thick were produced.

Materials prepared by the previous technique of spraying with volatile solvent
mixtures were highly susceptible to failures of the type shown in Figure 15
because of fiber alignment and layered flaws. Typically, the anisotropy ratio
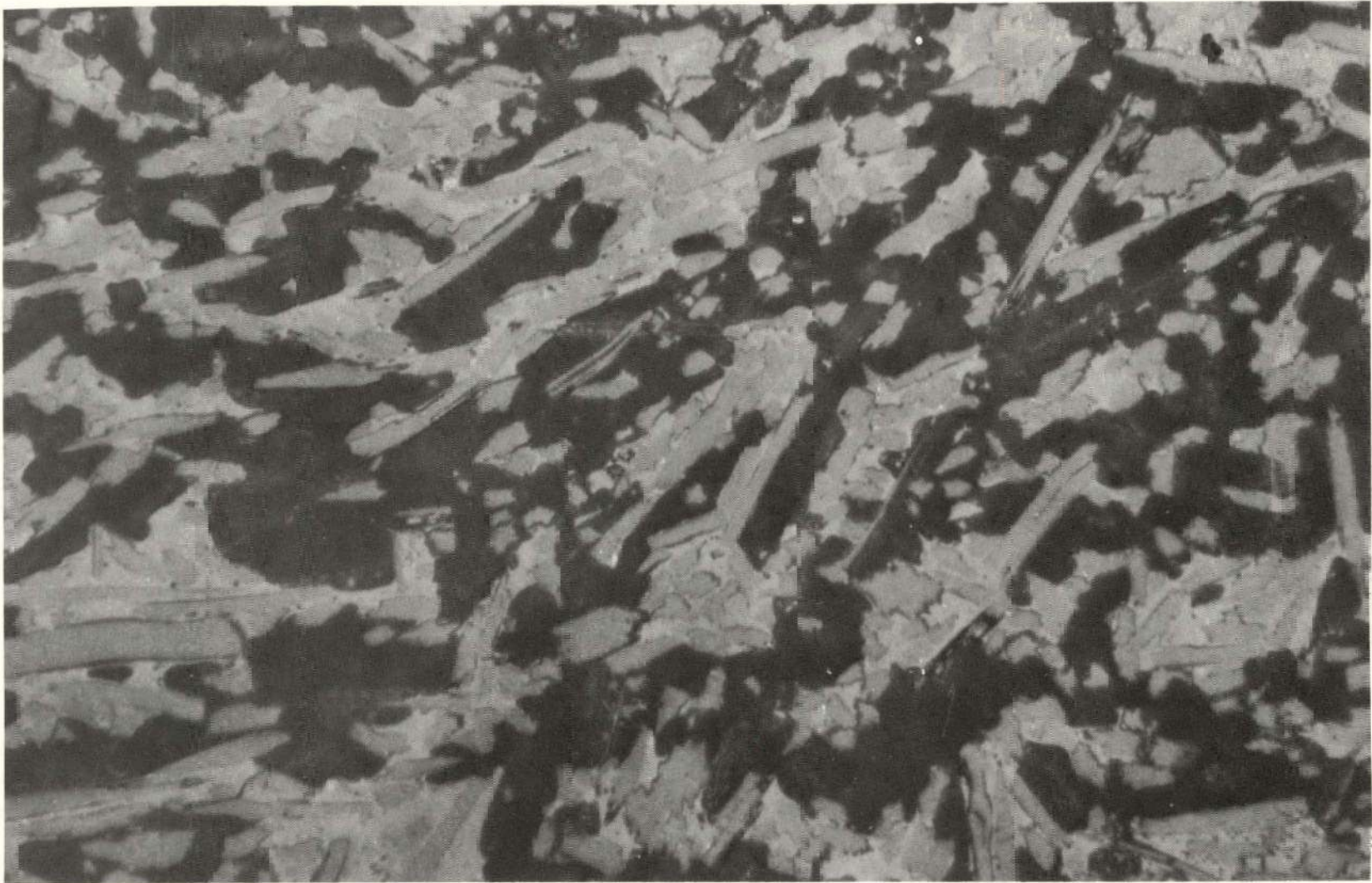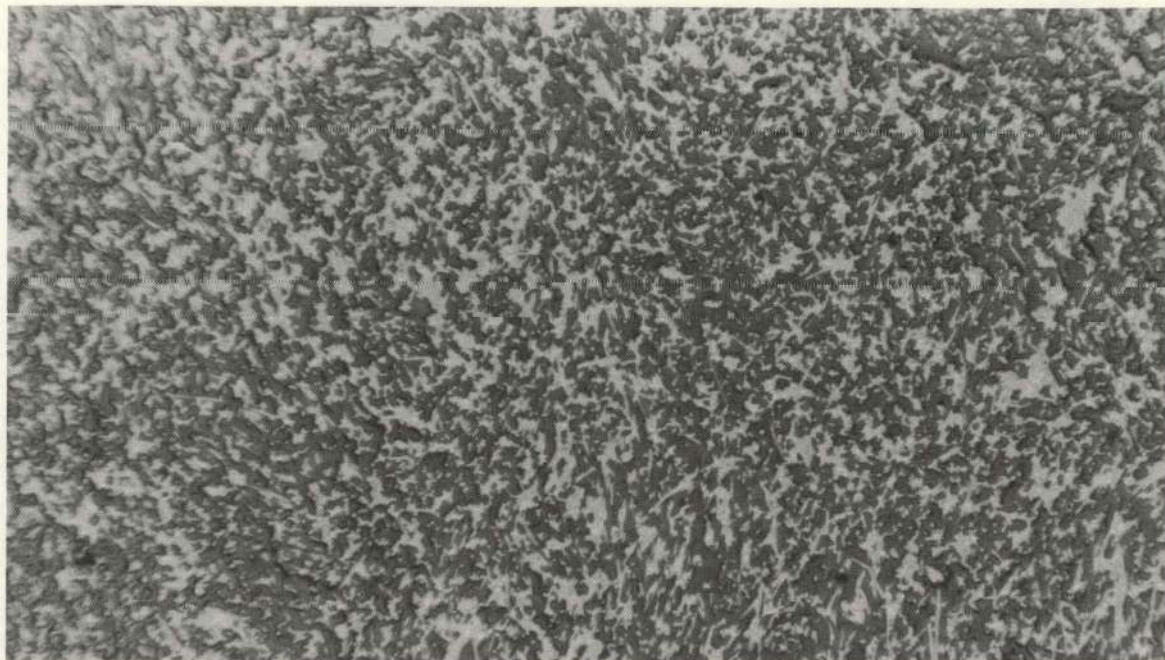(by CTE) for such material was 1.7/1.00, and shrinkage ratios (radial to

Figure 7. MICROSTRUCTURE OF FIBER-BINDER AGGLOMERATES IN A LOW-DENSITY (0.7 gm/cc) CAST CYLINDER. (500X)

(a) Axial View

(b) Radial View

Figure 8. MICROSTRUCTURES OF AN ISOTROPIC CASTING AFTER PRESSING AND CARBONIZATION AT ATMOS-PHERIC PRESSURE. (Density - 0.7 gm/cc, 100X)
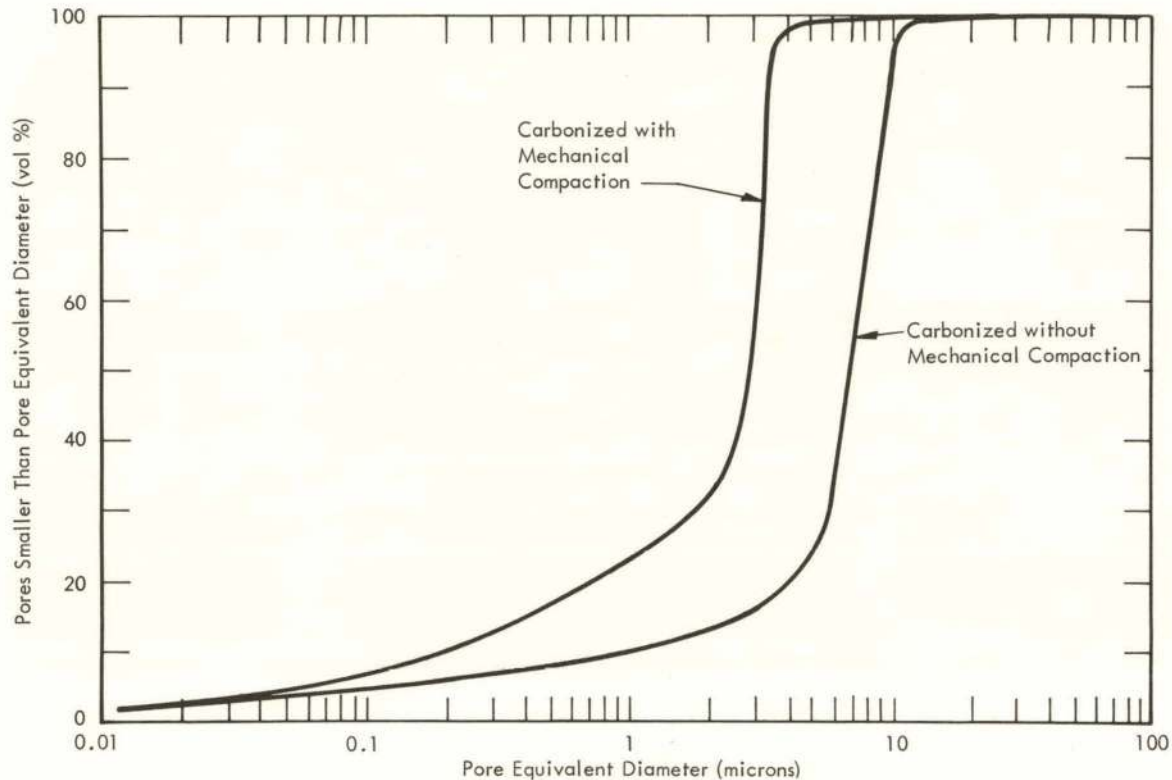
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Figure 9. TYPICAL PORE SPECTRA OF TWO TYPES OF ISOTROPICALLY PRESSURE CARBONIZED MATERIAL.

tangential) ranged from 3 to 10/1, depending on density. Cylinders with unfavorable wall thickness-to-diameter ratios (ID/OD ratios less than 0.75/1.00) were certain to fail by cracking or delamination, or both.

With this background of experience, the need for a more uniform and isotropic sprayed structure was indicated. After evaluation of several binders, it was determined that the starch-water slurry provided a fiber structure (Figure 16) which did not appear to be aligned. The addition of carbon black[f] to the spray mix in an amount which did not exceed the void volume between fibers yielded a structure with anisotropy ratios from 1.1 to 1.2/1.00. Cylinders prepared with this composition and with ID/OD ratios less than 0.65/1.00 have been densified by the schedule given in Table 1.

At the maximum density, the CTE ratio was 1.3/1.0, and the Bacon anisotropy factor was determined to be 1.2. From Figure 17 it appears that the fiber structure was not affected by densification to 1.6 gms/cc. The microstructure of this type of material at a density of 1.7 to 1.8 gms/cc is seen in Figure 18. Typical properties are listed in Table 2.

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(f) Thermatomic Carbon's Thermax.
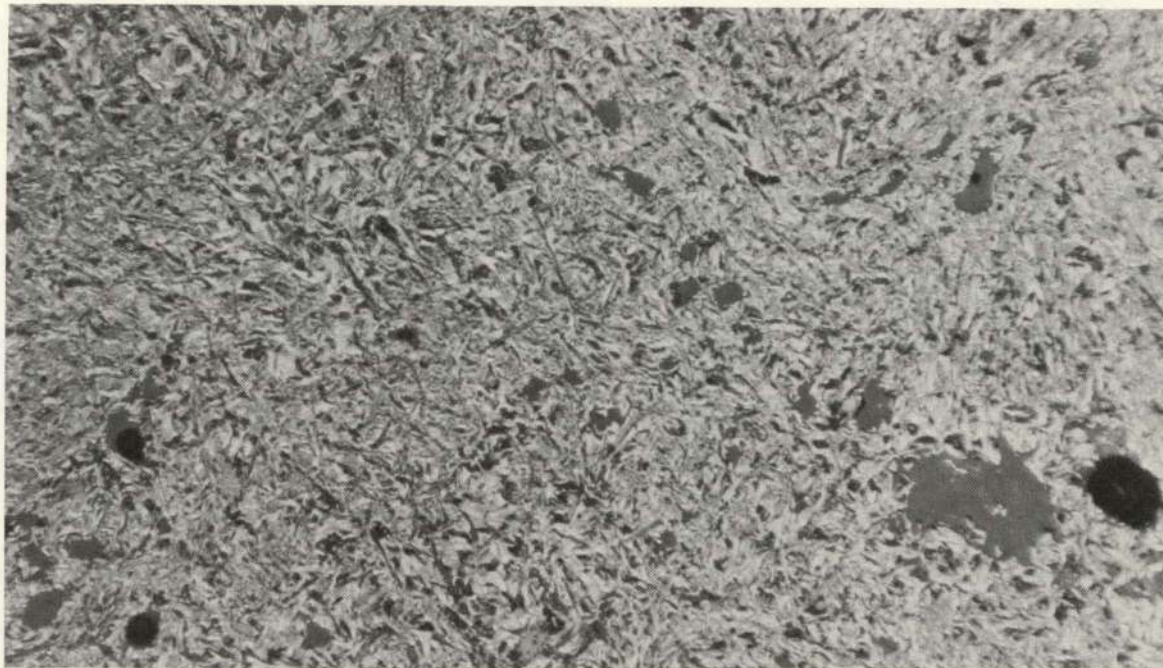
(a) 100X
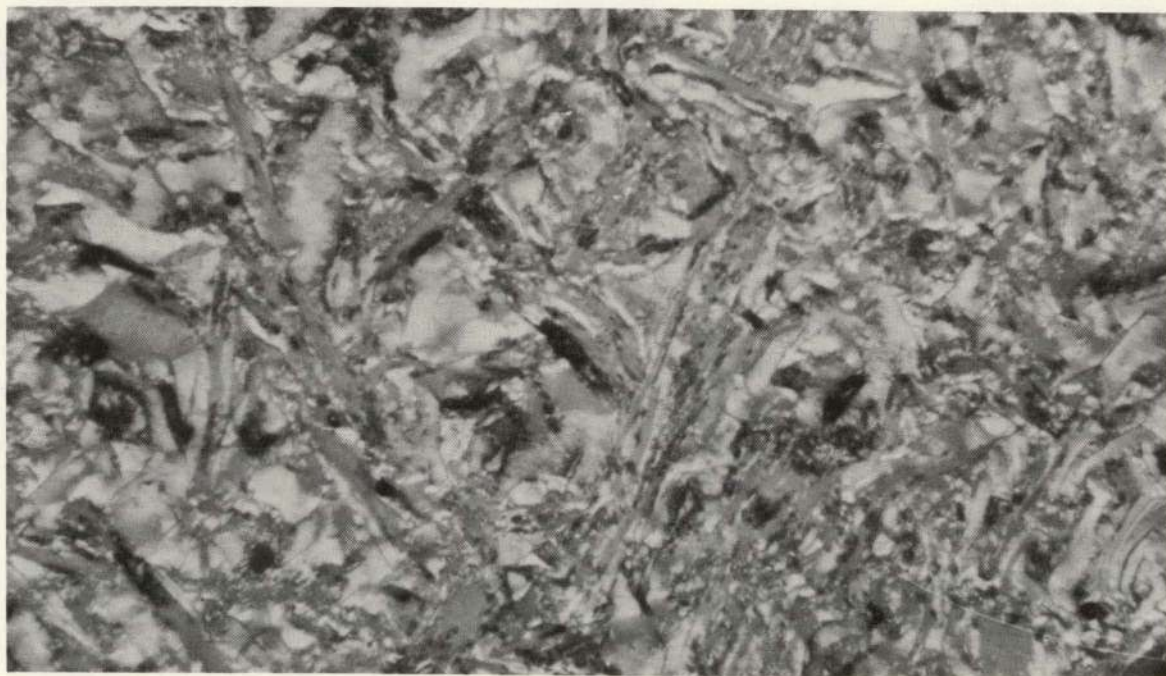
(b) 500X

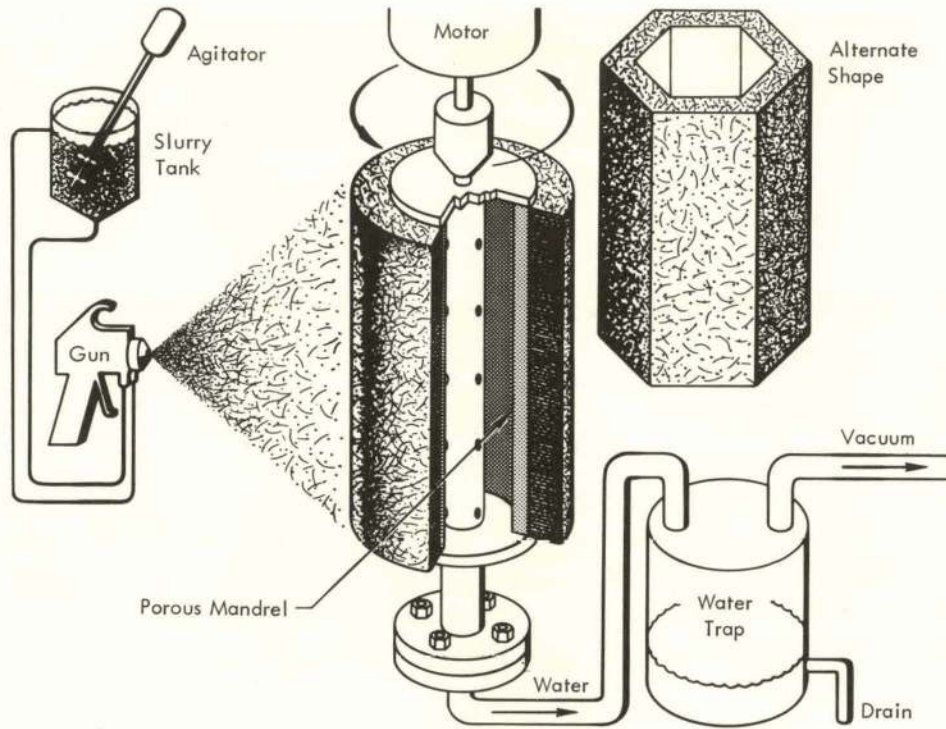Figure 10. MICROSTRUCTURES OF AN ISOTROPIC CASTING AT A DENSITY OF 1.75 gms/cc.

Figure 11. VACUUM-ASSISTED SPRAY LAY-UP TECHNIQUE.

Flock Lay Up

Figure 19 shows a schematic process for the electrostatic deposition or flock lay up of carbon fibers. Using very dilute binders (such as latex) between flocked layers, fibers have been deposited onto rotating cylindrical mandrels up to approximately two inches thick. Considerable difficulty was experienced in maintaining a uniform fiber density across the binder layer due to excess binder or inadequate penetration of fibers into the previous layer. This layer variation is presented in Figure 20. One of these low-fiber-density areas is shown after densification by CVD in Figure 21. The sample of Figure 21 was broken through the plane of the low-density area. This section of the sample is shown in Figure 22. Battelle has demonstrated that electrostatic deposition can produce thicknesses up to one inch without the use of an intermediate binder by the use of a reciprocating flat-plate collector.[6] During these studies, cylindrical shapes up to 0.5 inch in thickness were made by depositing a mixture of fibers and a fine particulate epoxy binder which was continuously thermoset.

Type of fiber and the length-to-diameter ratio were found to be important variables which influence the fiber orientation. In general, the larger-diameter, discrete, untangled, long fibers were preferentially oriented with axes normal to the surface
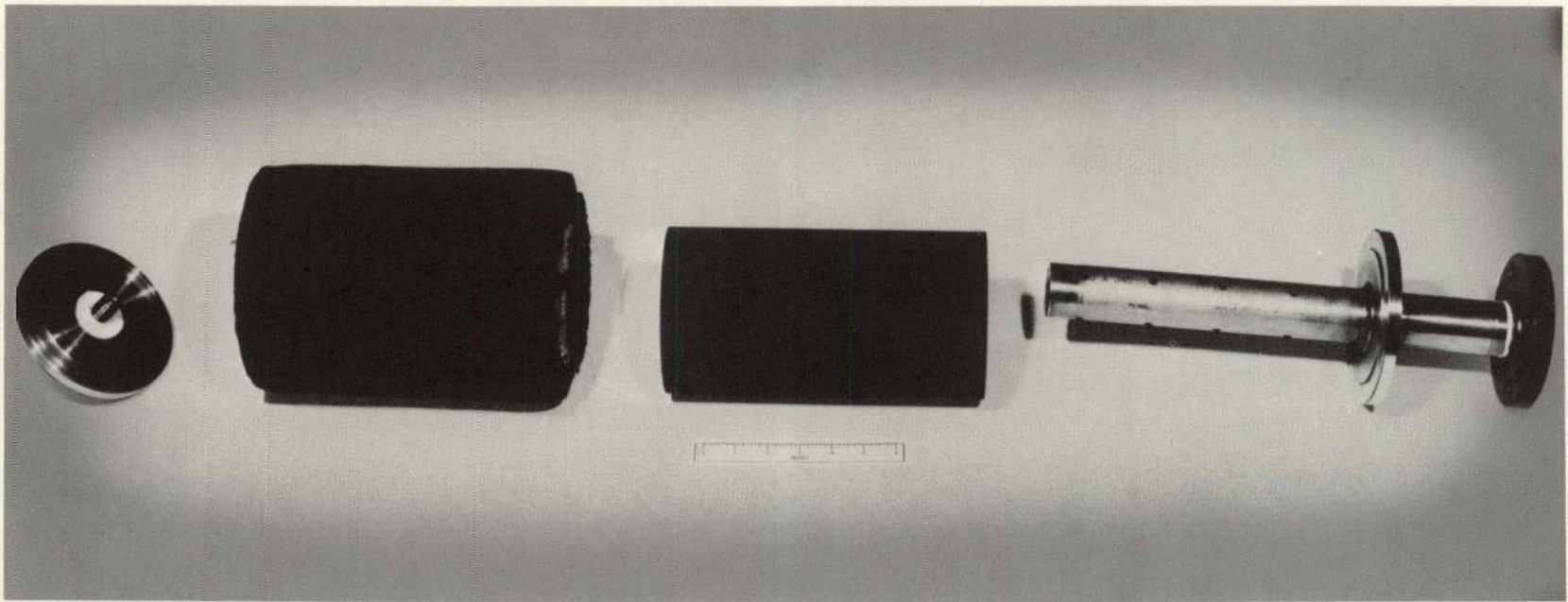
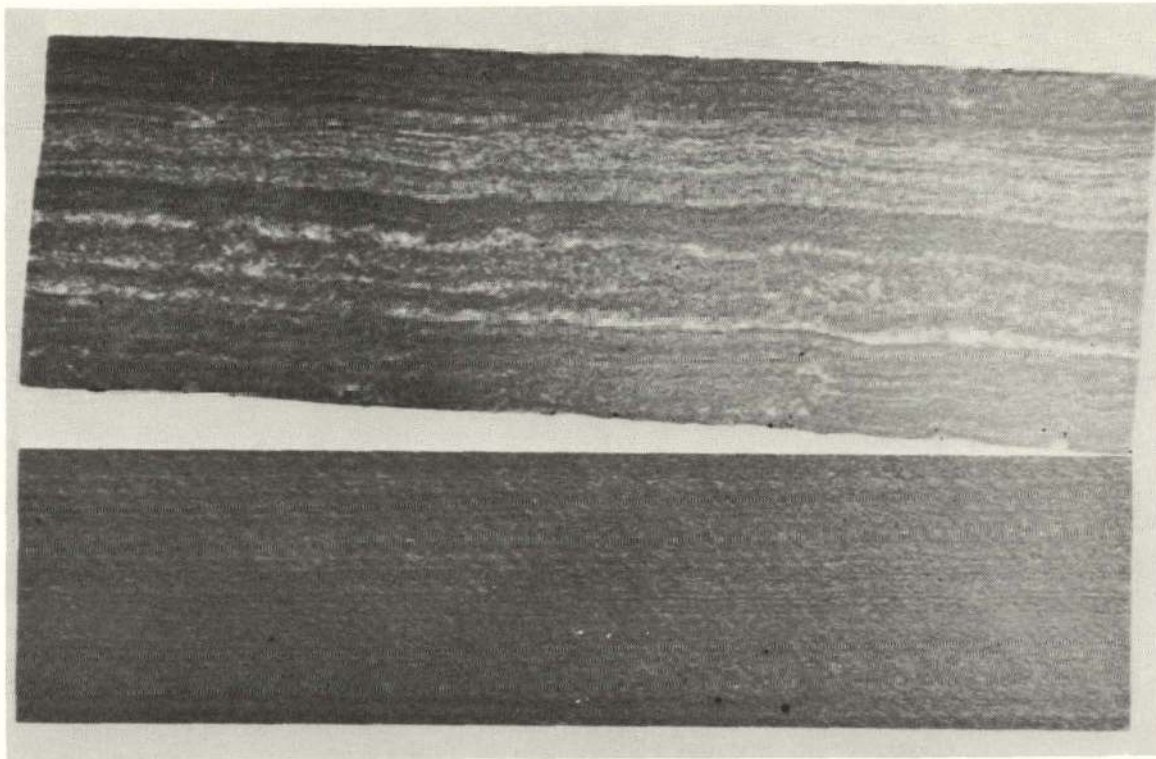Figure 12. AN EXPLODED VIEW OF A VACUUM CYLINDER MANDREL AND PART.

Figure 13. RADIOGRAPH OF A THIN SECTION OF SPRAY-FORMED MATERIAL PREPARED BY THE VOLATILE-SOL-VENT METHOD (TOP) AND THE VACUUM-ASSISTED TECHNIQUE (BOTTOM).

of the sample. Anisotropy factors as high as 1.40(g) were obtained on samples produced with these types of fibers. Small-diameter and short-length fibers were more randomly oriented by the process. For this type of fibers, an anisotropy factor of about 1.0 with a maximum value of only 1.06 was obtained. Generally, the potential of this technique has just been touched, but it has been applied and shows promise in combination with filament winding. Figure 23 shows a high-modulus (Thornel 50) filament yarn bundle surrounded by flocked two-micron-diameter fibers. Note the randomness of the flocked fibers and their ability to fill voids. Cylinders have been constructed by alternately winding and flocking layers, with the winding layers alternating between 0 and 90 degrees.

Pulp Molding

One of the most uniform methods for the orientation of fibers in planes parallel to the molding surface is shown schematically in Figures 24 and 25. Very dilute

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(g) If all fibers were deposited perpendicular to the surface, the anisotropy factor would increase.
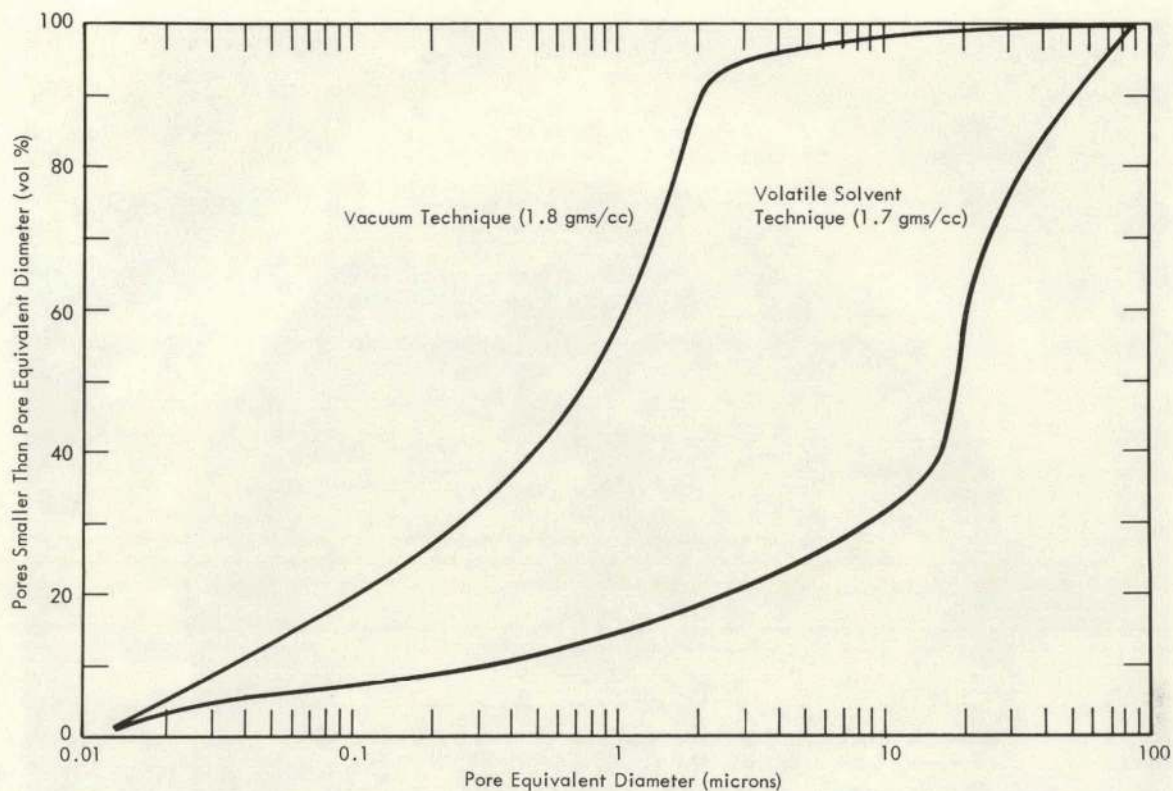
Figure 14. PORE DISTRIBUTIONS FOR SPRAY-FORMED MATERIALS PREPARED BY THE VACUUM-ASSISTED TECHNIQUE AND THE SOLVENT METHOD.

slurries of fibers and starch in water (eg, 0.3 wt % solids in water with a 1/1 fiber-to-starch ratio) were used to produce the fiber structures shown in Figure 26.

As indicated by the model of this technique (Figure 1) and Figure 26, a highly anisotropic fiber structure was expected. Anisotropy (CTE ratio) was near 2.0 for as-molded structures, and failures of the type shown previously (Figure 15) were frequently experienced during liquid impregnation and carbonization.

However, the fiber structures were very uniform in porosity and proved to be a good substrate for carbon-vapor infiltration. Figure 27 shows the microstructure after such an infiltration to a density of 1.6 gms/cc.

The infiltrated composites were not easily graphitized and, therefore, exhibited poor thermal shock resistance. This problem must be eliminated before fabrication, and application will be seriously considered.

The most important application of the pulp-molding technique was fabrication of thermal insulation. Flexibility of the process allowed the thermal conductivity
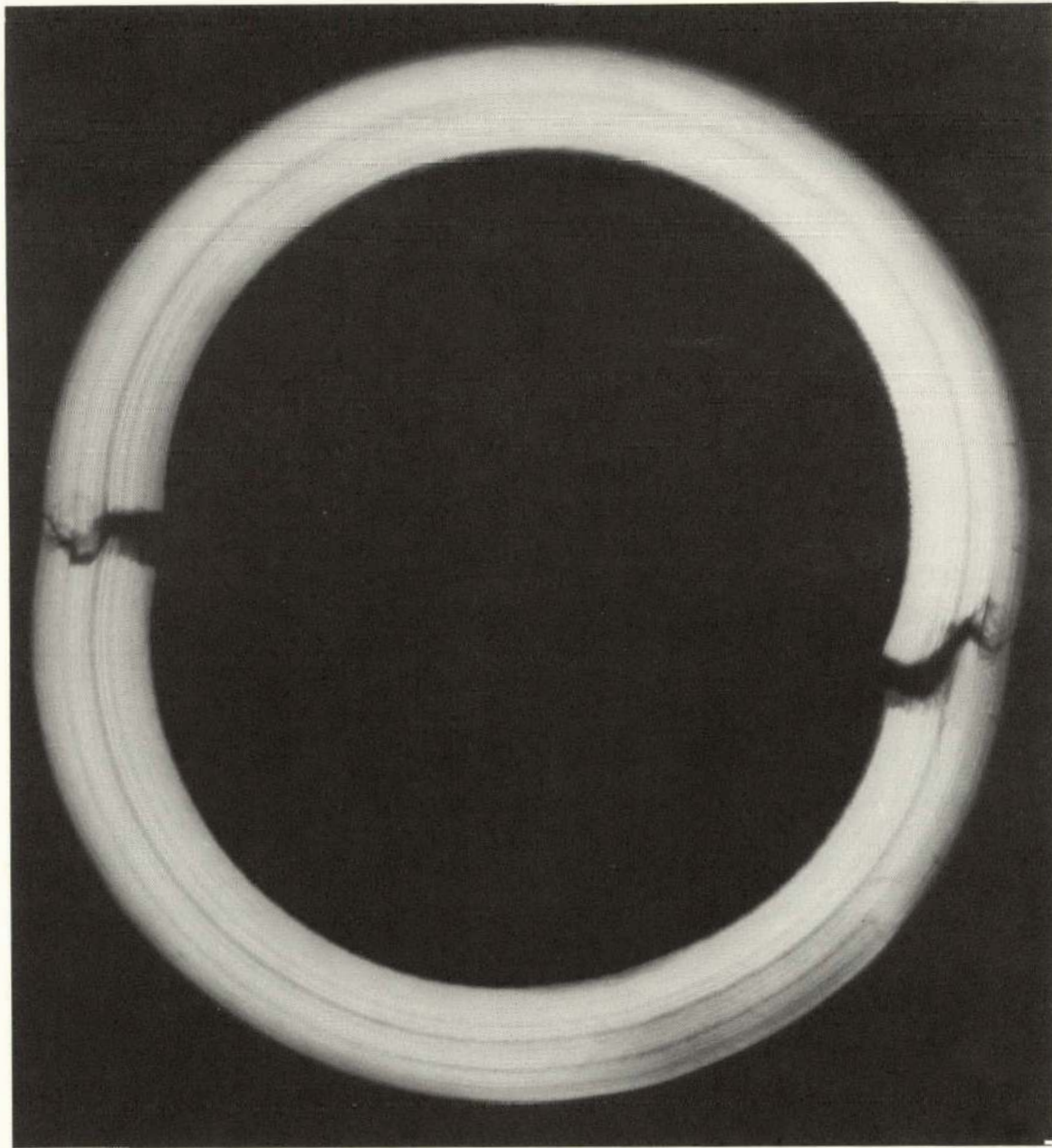
Figure 15. RADIOGRAPH OF A CYLINDER WHICH FAILED DUE TO ANISOTROPIC SHRINKAGE.

to be varied by as much as a factor of 10 and compressive strength by a factor of 100 by varying such processing variables as: fiber length, binder concentration, and fiber-packing density. Figures 28 and 29 show property trade-off curves for compressive strength, thermal conductivity, and bulk density. These thermal conductivities are comparable with Min-K at elevated temperature; and, due to the refractory nature of the carbon-carbon fiber composite, these insulation materials are useful for higher-temperature applications.

100X
300X
SM-3627
SM-3626

Plane Normal to the Spray Direction

300X
1000X
SM-3637
SM-3638

Plane Parallel to the Spray Direction - Sprayed Fiber Composite - SEM
(As Sprayed and Carbonized; Density - 0.20 gm/cc)

Figure 16. SCANNING ELECTRON MICROGRAPHS OF A FIBER STRUCTURE PREPARED BY THE VACUUM-ASSISTED
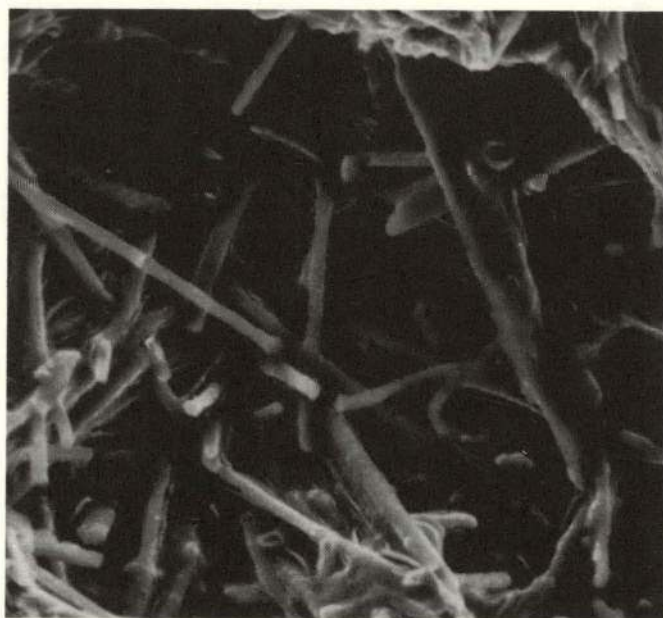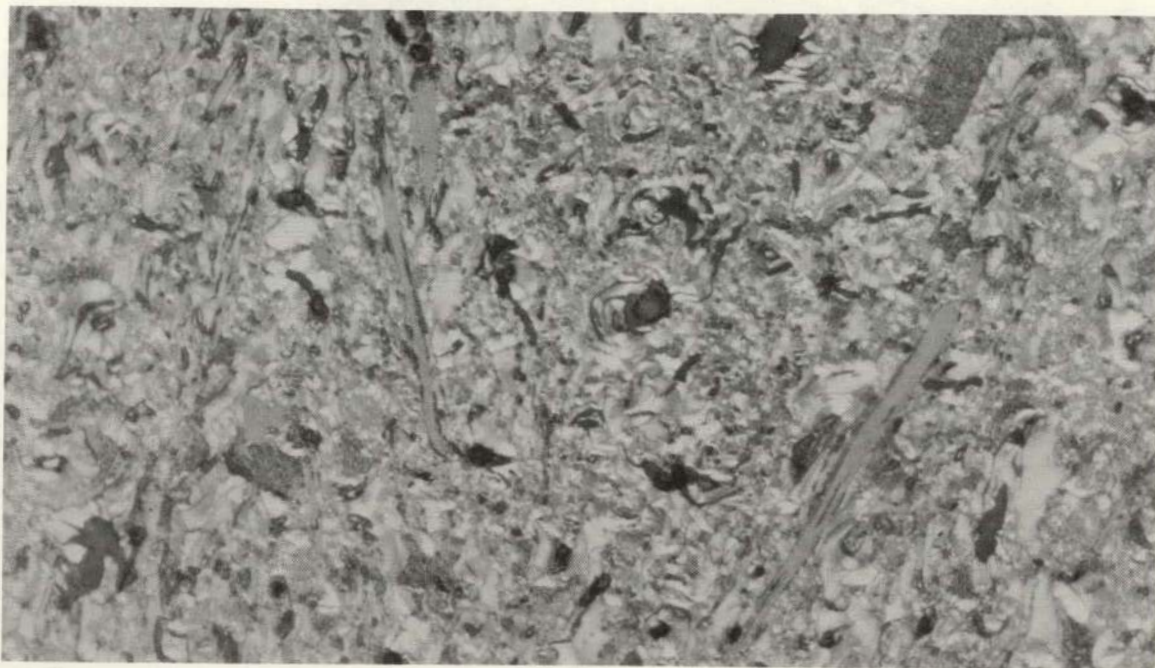SPRAYING TECHNIQUE.

28
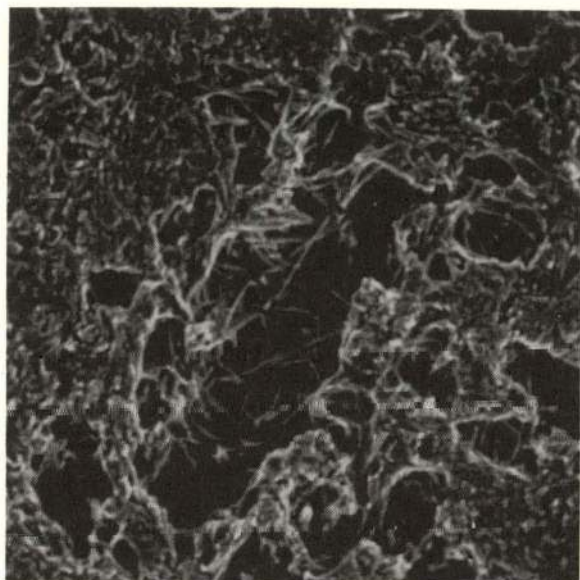
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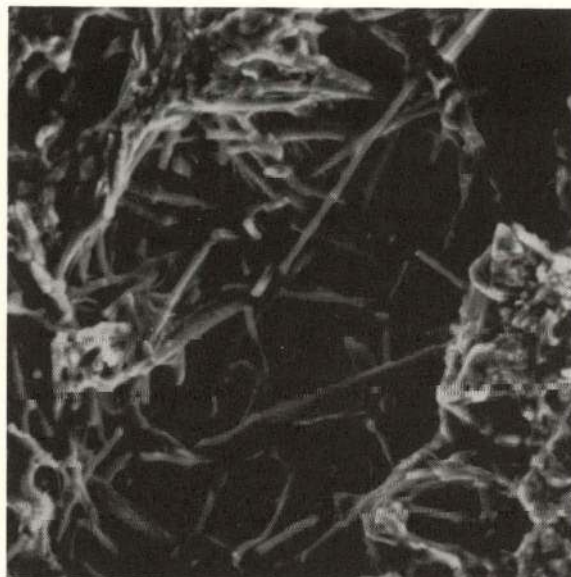
SM-8935

200X

SM-8934

300X

SM-8933

Figure 17. SCANNING ELECTRON MICROGRAPHS OF A VACUUM SPRAY-FORMED PART AFTER DENSIFICATION TO 1.6 gms/cc. (Viewed Normal to the Spraying Direction)

(a) 250X

(b) 500X

Figure 18. MICROSTRUCTURES OF DENSIFIED (1.8 gms/cc) MATERIAL PREPARED BY THE VACUUM-ASSISTED SPRAY TECHNIQUE AND PITCH IMPREGNATION.

Table 1

DENSIFICATION SCHEDULE

Sample Treatment	Bulk Density[1] (gms/cc)
As-Vacuum Sprayed and Carbonized to 1,000° C	0.3
Impregnation (25% pitch in benzene)[2]	0.57
Impregnation (50% pitch in benzene)	1.06
Vacuum Impregnation and Pressure Carbonization	1.51
Vacuum Impregnation and Pressure Carbonization	1.80

(1) Bulk density determined by mercury intrusion at a pressure which fills all pores larger than 100 microns.
(2) After each impregnation, the part was carbonized to about 1,600° C.

Table 2

TYPICAL PROPERTIES OF VACUUM SPRAY-FORMED SAMPLE

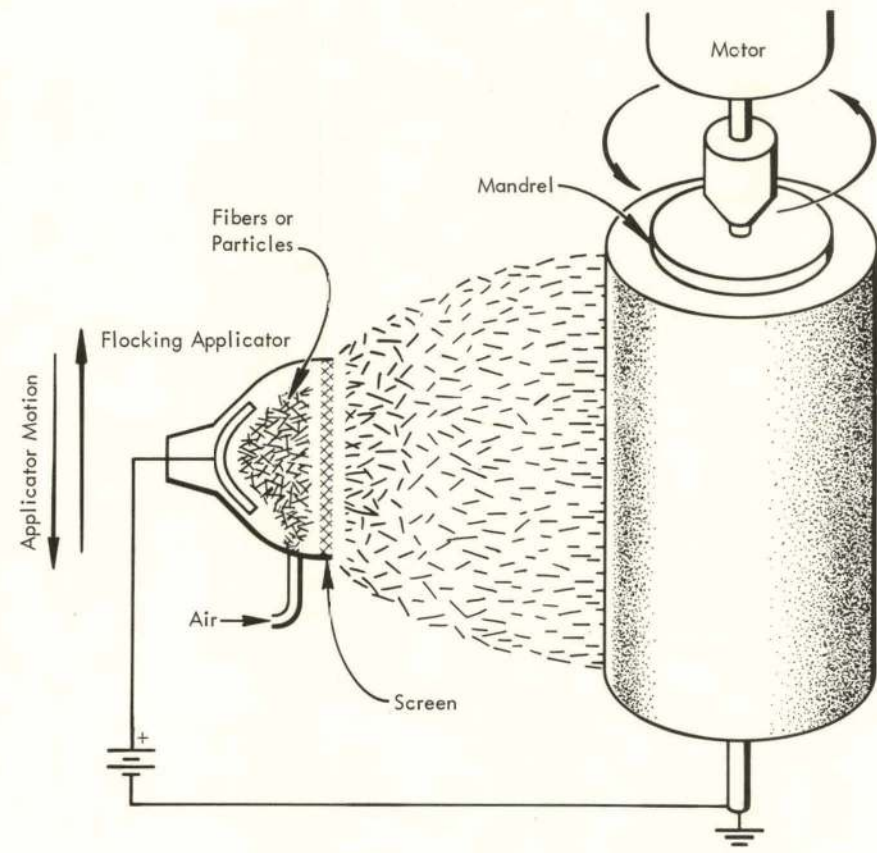|	
Tensile Strength (psi)	5,300
Sonic Modulus (10^6 psi)	1.7
Thermal Diffusivity (cm^2/sec)	1.3 – 2.2
Porosity (%)	15
Porosity for Pores Less Than 10 Microns (%)	98
Radial Thermal Expansion Coefficient (° C^{-1})	1.0×10^{-6}
Axial Thermal Expansion Coefficient (° C^{-1})	1.3×10^{-6}

Figure 19. FLOCK LAY-UP PROCESS.

Figure 20. FLOCKED-FIBER DENSITY VARIATION.

(a) 50X

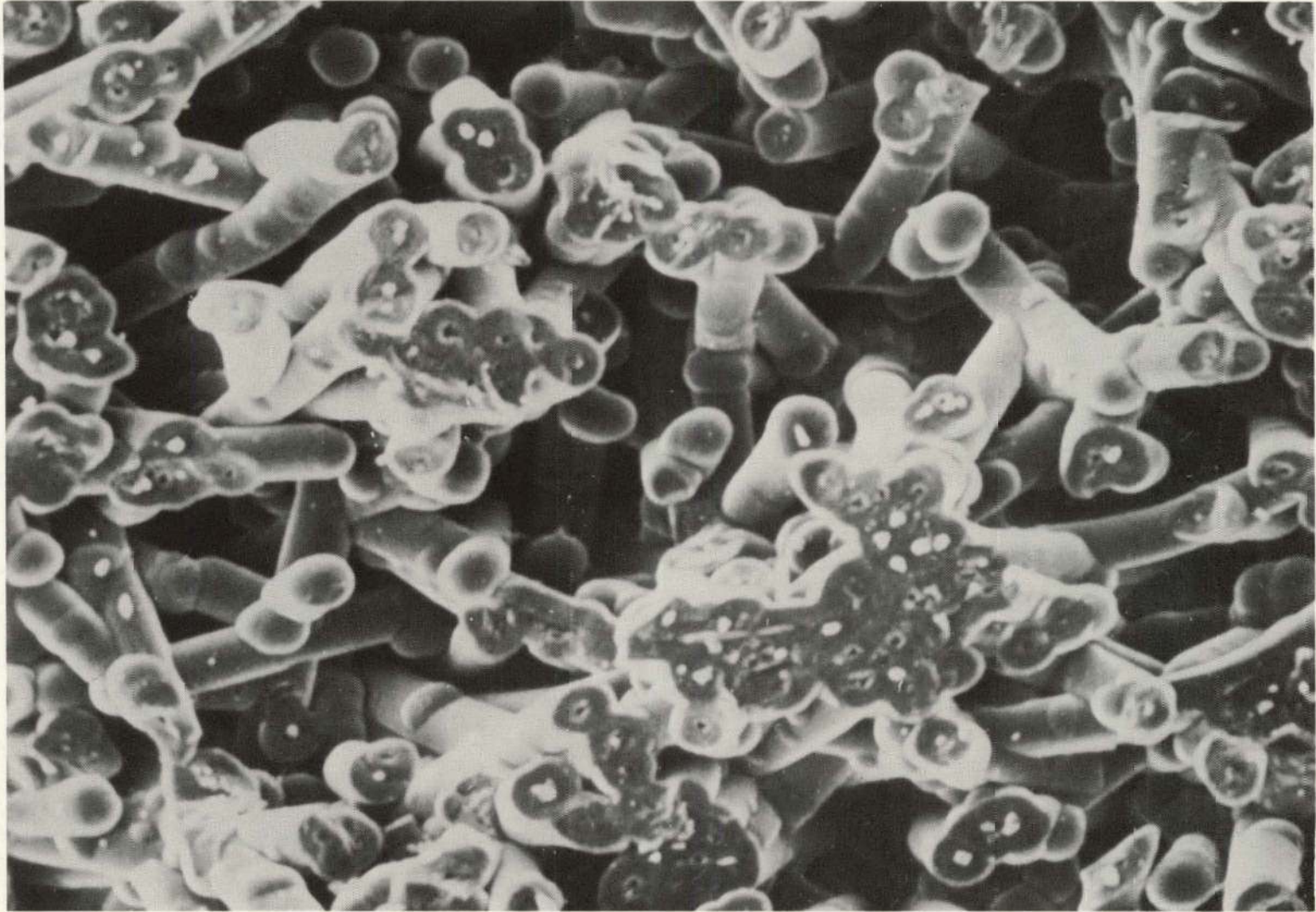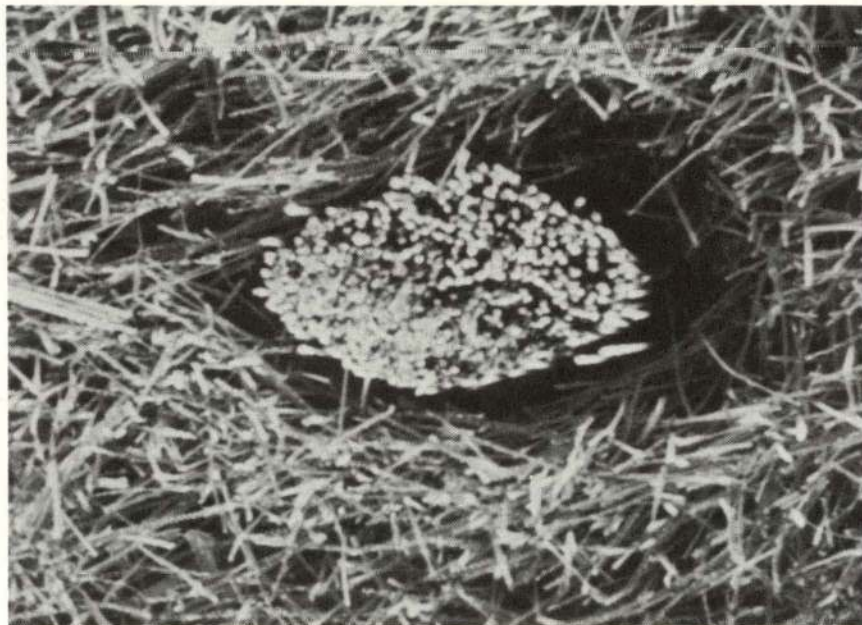(b) 150X

Figure 21. DENSITY VARIATION AFTER DENSIFICATION.

Figure 22. LOW-DENSITY VARIATION IN A FLOCKED SAMPLE.

33

34

(a) 55X

(b) 60X

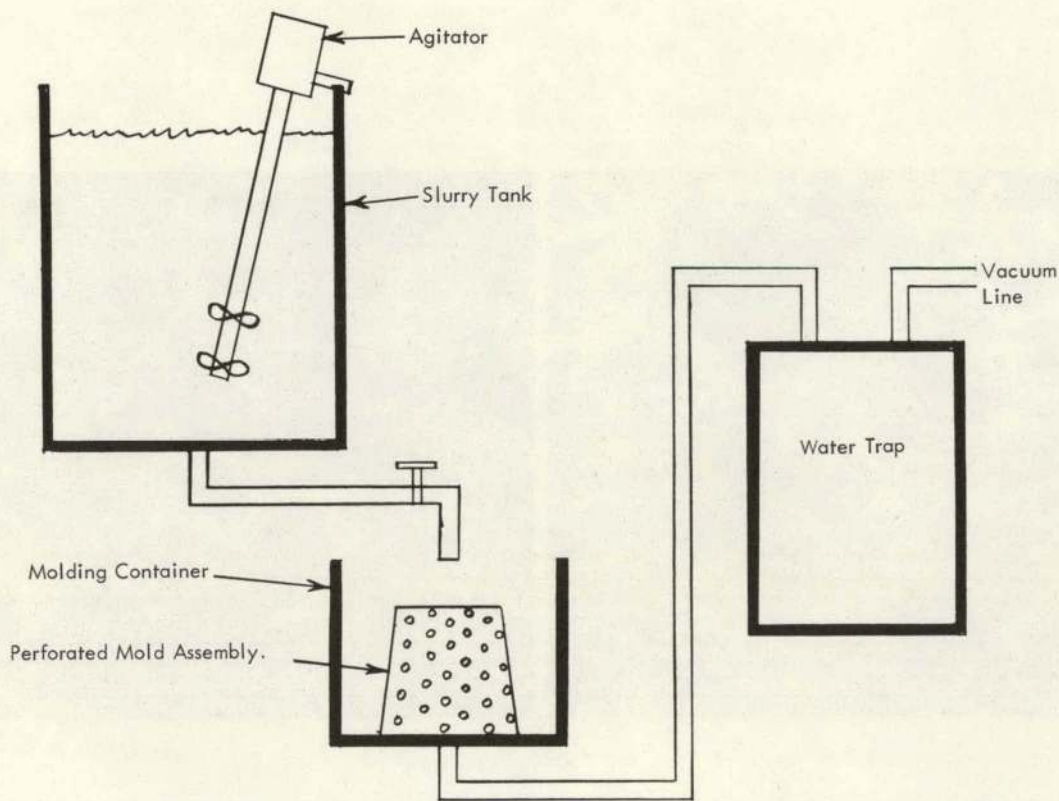Figure 23. FILAMENT-WOUND YARN BUNDLES SEPARATED BY FLOCKED FIBERS.
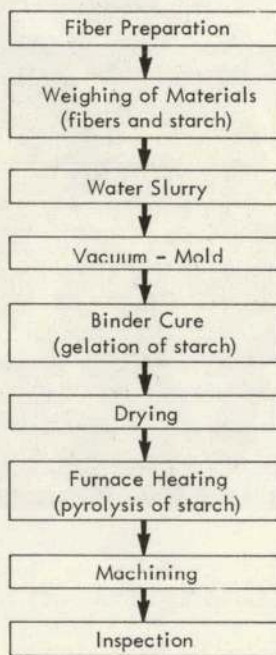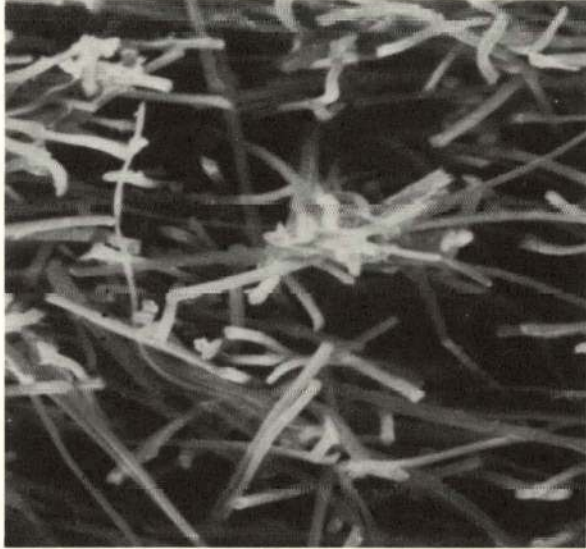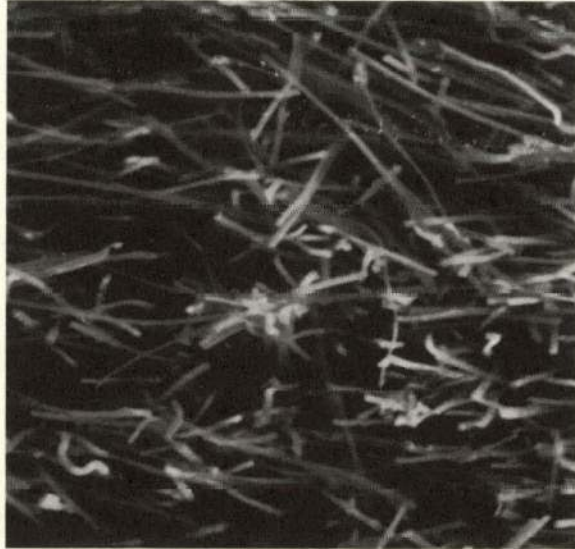
Figure 24. PULP MOLDING PROCESS.

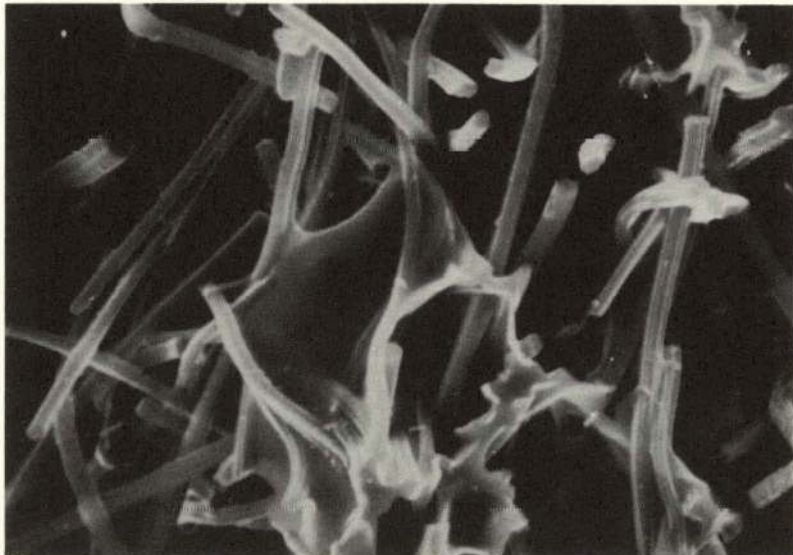Figure 25. PROCESS FLOW CHART FOR PULP MOLD-ING.

150X

SM-3544

50X

SM-3543

1000X

SM-3713

Figure 26. SCANNING ELECTRON MICROGRAPHS SHOWING WEB BOND IN THE PULP-MOLDED STRUCTURE.

(a)

(b)

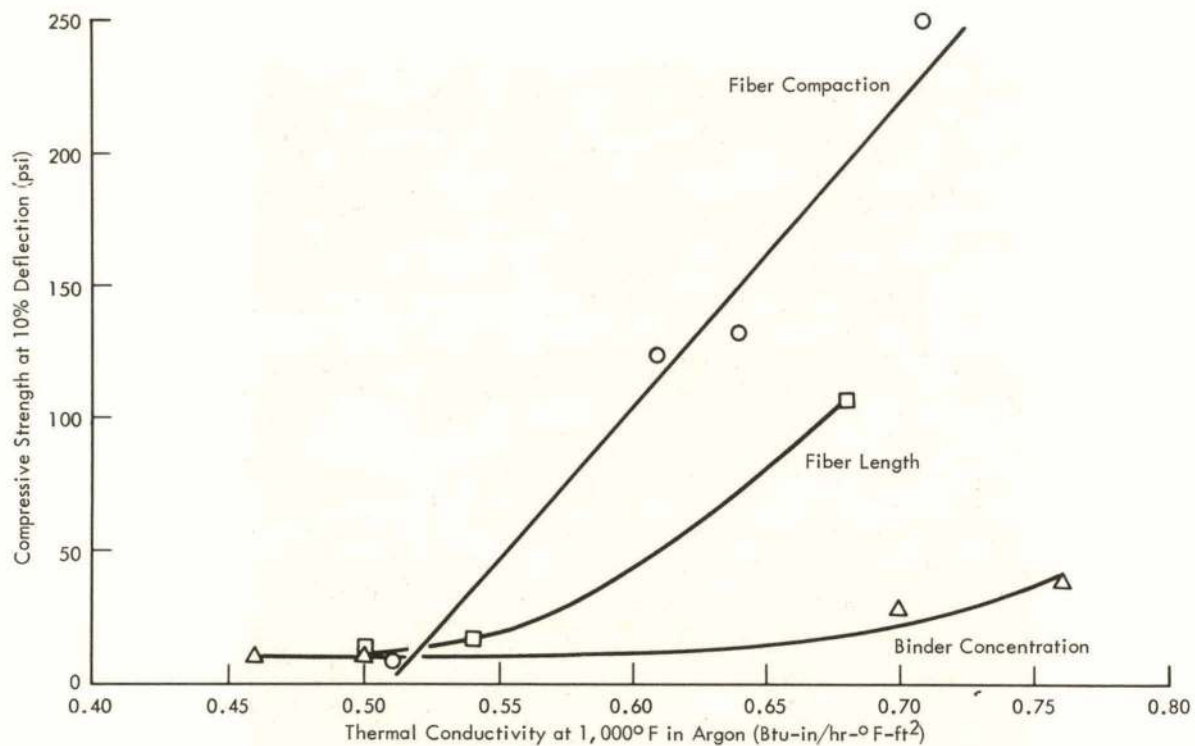Figure 27. PULP MOLDED AND CARBON VAPOR INFILTRATED TO A DENSITY OF 1.6 gms/cc. (250X)

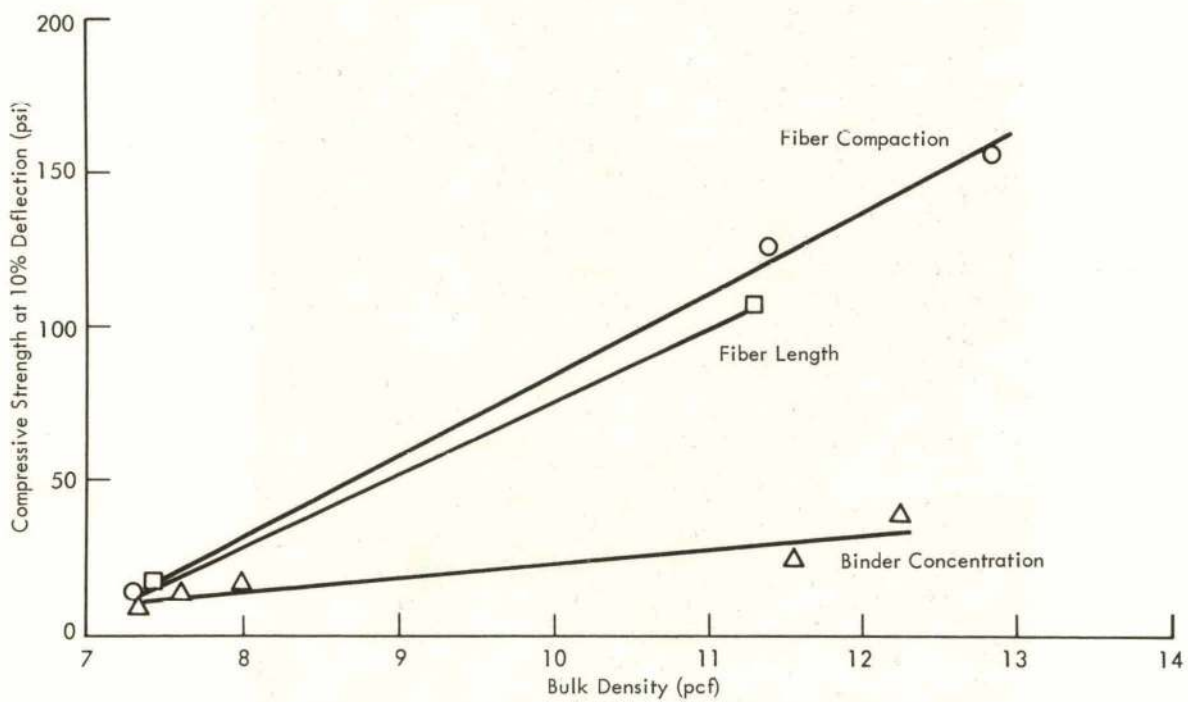Figure 28. PROPERTY TRADE OFFS RESULTING FROM SEVERAL MATERIAL AND PROCESS PARAMETERS. (Thermal Conductivity)

Figure 29. PROPERTY TRADE OFFS RESULTING FROM SEVERAL MATERIAL AND PROCESS PARAMETERS. (Density)

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