

# EFFECTS OF MATRIX AND PROCESS VARIATIONS ON PROPERTIES OF 3-D CARBON-CARBON COMPOSITES

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## Introduction

Considerable latitude exists for designing carbon-carbon composites with prespecified performance attributes suitable for reentry vehicle components, including nose tips, heat shields, and rocket nozzles. This can be done via selection of fibrous reinforcement properties and construction and by choice of matrix precursor materials and processing conditions. Under this program, three-dimensionally woven graphite yarn preforms were densified to yield carbon-carbon composites, using various matrix precursor materials and processing conditions. Effects of process modifications on process efficiency (density gain per cycle) and volume increase of the composites and on the final bulk density, open porosity, and permeability were assessed.

## Experimental and Results

Sixteen carbon-carbon composites (Table 1) were processed from 3-D fibrous preforms woven by Fiber Materials, Inc., from Thornel 50 yarns in an orthogonal 2-2-3 construction (shown in Ref. 1). The dimensions of billets 697 and 676 were approximately 4 x 4 x 8 in., and the other 14 billets were approximately 2 to 16% of this volume. The baseline process was multiple cycles of (1) coal tar pitch impregnation, (2) pyrolysis at 1,000 psig (300 psig for the first three cycles), and (3) graphitization in argon to 2,800°C. The pyrolysis temperature was 675°C for the initial pitch cycle and 1,000°C for all other cycles. The matrix was Allied Chemical CP275-Grade 15V coal tar pitch. The pitch was pre-heat-treated for all impregnation cycles except the initial one, to increase char yield.

Modifications included carbon vapor deposition (CVD) steps, resin densification steps, pyrolysis and graphitization temperature variations, and extra densification (impregnation plus pyrolysis) and graphitization cycles. For CVD, methane at 1,100°C was employed either at the beginning of processing (initial CVD) or following the second pitch densification step (intermediate CVD). For intermediate resin processing, two ENF resin densification steps were conducted after the second pitch densification step, or if an intermediate CVD step was employed in the same billet, two steps after the CVD step. For final resin processing, the final three densification steps were with ENF resin. ENF is 50-50 mixture of Dow Chemical DEN 438 epoxy novolac resin and Quaker Oaks furfuryl resin precursor. The 2,400°C, 2,800°C, or 3,100°C heat treatments in argon were conducted after each densification step except the initial one or the first of two intermediate resin cycles. The time above 2,500°C was 3 and 6 hours for each 2,800°C and 3,100°C cycle, respectively. For graduated increases in pyrolysis temperature, the temperatures for the

second and third pitch cycles were 775°C and 875°C, respectively, and the first 2,800°C graphitization cycle followed the fourth pitch densification cycle.

Table 2 summarizes process efficiency, degree of "overprocessing" past maximum composite density, volume increase, and selected physical properties of the 16 materials. The viscous permeability coefficient was determined from measurements of nitrogen flow through the composite in the 3-D weave Z direction. Figure 1 depicts typical in-process property changes for material BB-2. In addition, detailed microstructural examination and mechanical, thermophysical, and ablative testing was done. Some results of these latter evaluations are being reported by J. Jortner at this conference and will be referred to in the discussion.

## Discussion

The composites increased in volume during processing, particularly during later process steps when the density was high. The linear growth tended to be larger in the X and Y directions than in the Z direction, a consequence of the unbalance of the 2-2-3 weave. Analyses of the growth mechanisms have been reported in Ref. 1 and by L. B. Greszczuk at the present conference. The magnitude of the growth appears to be dependent on processing details and varied between nearly zero and 13% volume change. The growth can limit or decrease the ultimate density of the composite as the volumetric increase can equal or exceed the mass increase in the last process cycles (Figure 1). Potential devices for limiting growth are intermediate resin processing, high-temperature graphitization, and reduced maximum temperatures for early process cycles.

Graphitization to 3,100°C appeared to improve process efficiency. Within the three groups of no CVD, intermediate CVD, and initial CVD, the 3,100°C variations all had relatively high bulk densities, high thermal diffusivities, decreased room-temperature strength, and improved ablation performance. The 2,400°C heat treatment resulted in poor process efficiency and decreased mechanical properties (excepting shear strength). Multiple final graphitization cycles resulted in increased cracking and decreased ablative performance.

Intermediate resin cycles produced increased process efficiency, decreased apparent density, decreased macropore size, and improved off-axis strength. Microscopy revealed that the resin tends to produce a carbon matrix that occupies the interior area of weave pockets or large pores rather than coat the outer edges (as pitch processed at 1,000 psig does), thus increasing the composite internal surface area available for further pitch deposition and resulting in

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Most of the comparative density and porosity improvement of material 676 relative to material D occurred near the end of processing, possibly indicating an improved ability of liquid pitch to remain in larger composites during the late carbonization cycles when the paths for penetration are narrow. The baseline low-pressure pitch process provides reasonably high process efficiencies until the composite porosity is reduced to approximately 15%. Thereafter, either increased process pressures (e.g., 15,000 psig) or modifications such as intermediate resin cycles are needed to achieve high efficiencies.

The contributions of C. R. Rowe of the Naval Surface Weapons Center and D. A. Eitman and J. Jortner are acknowledged.

1. Jortner, J. Cracking in 3D Carbon-Carbon Composites During Processing and Effects on Performance. Army Symposium on Solid Mechanics, Cape Cod, Mass, 14-16 Sept 1976.

Code	Process Variations	ND <sup>†</sup>	NG <sup>†</sup>
697 <sup>†</sup>	Baseline Pitch, Large Block	13	12
676	Baseline Pitch, Large Block	15	14
D	Baseline Pitch, Small Block	15	14
A	Graduated Increases in Pyrolysis Temperature	18	15
DD	Three Added Cycles (Relative to D)	18	17
R	Intermediate Resin Impreg- nation	16	14
RR	Intermediate and Final Resin Impregnation	13	11
B	Low-Temperature Heat Treatment (2, 400° C)	18	17
C	High-Temperature Graphitization (3, 100° C)	16	15
DM	Three Graphitization Cycles at Completion of Processing	15	16
BB-1	Intermediate CVD	16	15
BB-2	Intermediate CVD and Intermediate Resin	16	14
BB-3	Intermediate CVD and High- Temp Graph (3, 100° C)	15	14
BC-1	Initial CVD	14	14
BC-2	Initial CVD and Intermediate Resin	14	13
BC-3	Initial CVD and High-Temp Graphitization (3, 100° C)	13	13

\*Billet 697 was processed separately from the other materials during early process cycles.

Code	Densifications to 1.87 g/cm <sup>3</sup> Bulk Density	Densifications/Graphitizations/Past Maximum Density	Volume Increase %†	Block Data†			Specimen Data†			Viscous Permeability Coefficient 10 <sup>10</sup> in <sup>-2</sup>
				ρ <sub>B</sub> g/cm <sup>3</sup>	ρ <sub>A</sub> g/cm <sup>3</sup>	P %	ρ <sub>B</sub> g/cm <sup>3</sup>	ρ <sub>A</sub> g/cm <sup>3</sup>	P %	
697	10	0/0	4	1.92	2.07	7.5	-	-	-	0.7
676	12	0/0	8	1.94	2.09	7.3	-	-	-	-
D	13	0/0	3-9	1.91	2.10	8.9	1.91	2.12	10.0	1.6
A	14	2/2	2	1.90	2.07	8.4	1.90	2.11	10.1	3.8
DD	13	2/2	13	1.92	2.08	8.2	1.91	2.12	10.0	0.7
R	11	0/0	2-7	1.91	2.07	8.2	1.91	2.10	9.3	1.2
RR	11	0/0	0-3	1.90	2.06	7.4	1.91	2.08	8.3	7.1
B	15	2/2	7	1.88	2.06	8.7	1.87	2.10	11.0	0.7
C	10	0/0	4	1.94	2.09	7.3	1.94	2.12	8.6	11.2
DM	13	0/2	10	1.88	2.11	11.2	1.88	2.12	11.5	0.2
BB-1	13	2/2	5	1.88	2.06	8.9	1.89	2.11	10.1	2.0
BB-2	11	1 or 2/1 or 2	4	1.90	2.05	7.3	1.91	2.06	7.3	0.6
BB-3	10	0/0	8	1.92	2.07	7.6	1.93	2.11	8.5	2.0
BC-1	-	2/2	6	1.83	2.04	10.0	1.83	2.05	11.7	0.5
BC-2	11	2/2	N. D.	1.87	2.02	7.3	1.88	2.07	9.2	0.6
BC-3	10	2/2	N. D.	1.87	2.06	8.1	1.89	2.08	10.1	0.6

†  $P_B$  - Bulk density.  $P_A$  - Apparent density (ASTM C-20 water immersion for blocks; helium pycnometry for specimens).  $P$  - open porosity calculated from bulk and apparent densities.

