

## MECHANICAL PROPERTIES OF PITCH FIBER CARBON-CARBON COMPOSITES

Charles R. Rowe (Naval Surface Weapons Center, Silver Spring, MD)  
Louis L. Lander (Fiber Materials, Inc., Biddeford, ME)

### Introduction

A new class of carbon fiber reinforced carbon composites utilizing pitch-based carbon fibers are being developed for applications that require high strength at temperatures greater than 3000°C. These applications, such as rocket nozzles, aircraft brakes, and reentry vehicle nosetips, have depended upon rayon-based carbon fibers, but with uncertainty of future rayon supply, alternate fibers are needed. Pitch-based carbon fiber is one alternative.

The knowledge of processing and weaving variables on the properties of carbon-carbon composites has advanced substantially in the past few years. However, because the broad base of knowledge about carbon-carbon composites was developed for rayon-based fibrous reinforcement, it does not necessarily apply to pitch-based composites. Therefore, it is the purpose of this work to determine the effects of carbonization and graphitization temperatures, pyrolysis pressure, and type of carbon matrix on the mechanical properties of pitch fiber composites.

### Experimental

Union Carbide Corp. (Parma, Ohio) manufactured the fiber used for the composites for this study.

The fiber was woven into twelve three-dimensional performs in which the fiber was arranged in three mutually orthogonal directions designated X, Y, and Z. Figure 1 shows the dimensions of a unit cell of the preforms in which the distances between fiber bundles are indicated. The preforms, woven by Fiber Materials, Inc. (Biddeford, Maine), were 5cm x 5cm x 13cm.

To determine the effect of process variables on the mechanical properties of pitch fiber composites, a baseline process and eleven variations were selected to isolate process effects. The baseline process involved impregnation with petroleum pitch, A240 (Ashland Oil Co., Ashland, KY) followed by initial carbonization up to 900°C and graphitization to 2600°C in an inert atmosphere. This was followed by repeated impregnation, carbonization to 535°C at 34.5 MPa (5,000 psi), and graphitization to 2600°C. Approximately six such cycles were required to reach a density 1.95 g/cc. Table 1 summarizes the composites that were fabricated.

The mechanical properties determined on each composite included tensile, compressive, and flexure strength, modulus and strain. These measurements were made at room temperature in the Energy Materials Testing Laboratory (Fiber Materials, Inc.).

### Results

Mechanical data for the composites are summarized on Table 2 which list the maximum, minimum, average, standard deviation, coefficient of variation, and number of data points for each type of test. Results indicate there are wide ranges of some properties such as X/Y flexure modulus, 26.3 to 120 GPA (3.81 to 17.4 msi, Cv = 0.39). However, some properties, such as tensile strength, varied a small amount, 154

to 197 MPa (22.4 to 28.6 ksi, Cv = 0.06) for all process variations.

### Discussion

In order that the effect of each process variables on the mechanical properties, two parameters were selected to compare the composites for their resistance to thermal stress and impact. A thermal stress parameter,  $T = \frac{\sigma \cdot K}{E \cdot \alpha}$  where

$\sigma$  = strength  
 $E$  = modulus  
 $K$  = thermal conductivity  
 $\alpha$  = coefficient of thermal expansion

has been used to rank graphites. If the assumption is made that the conductivity and expansion of these materials are independent of process variables, then  $T = \sigma/E$ .

Impact resistance is approximately equal to the area under the stress strain curve,  $I = \sigma(\epsilon/2)$ , where  $\epsilon$  = total strain. For brittle materials  $\epsilon = \sigma/e$ , hence  $I = \frac{\sigma^2}{2E}$ .

Each parameter was calculated for all composites at the various test conditions. The effect of each process variable was determined by comparing the parameters for that process variable with the mean and standard deviation of all composites by the equations:  $T' = \sum \left( \frac{T - \bar{T}}{s} \right)$   $I' = \sum \left( \frac{I - \bar{I}}{s} \right)$

In both equations a positive number indicates a composite better than the average of all the composites.

The effect of each processing variable on the mechanical properties of pitch fiber composites is shown by plotting R, the average of T' and I', as a function of the process variables. Figure 2 shows the effect of the type of matrix on the properties of the composites. Petroleum pitch (A240) and coal tar pitch (15V) are approximately equal but the low sulfur petroleum pitch (LS24) is much worse. Also, the composites with CVD carbon are better than those without it. CVD carbon gave the composites essentially the same tensile strength as the composites without CVD carbon (7% less for LS24 and 6% more for A240), but lower moduli (-41% for LS24 and -16% for A240).

The importance of the initial carbonization temperature is shown in Figure 3, which indicates that low temperature is better than high initial carbonization temperature.

Figure 4 shows that there is a slight upward trend of R for graphitization temperatures above 2600°C (27% higher than the baseline). However, lower graphitization temperatures has a definite adverse affect. Higher graphitization temperatures gives better alignment of graphite crystallites.

The effect of pyrolysis temperature pressure is shown in Figure 5. It is apparent that pyrolysis at pressure less than 34.5 MPa (5000 psi) yield composite properties worse than the average. On the other

hand, for pressures greater than 34.5 MPa there is little difference up to 103 MPa (15,000 psi).

### Summary and Conclusions

It has been found that carbon-carbon composites reinforced with pitch-based carbon fibers can be fabricated with wide variations of processing conditions. The trends in thermal stress and impact resistance indicate that composites with CVD carbon are better than those composites without it. The CVD carbon appears to affect the alignment of graphite layer planes; that is, the presence of a small amount ( $V_F=0.11$ ) causes less formation of highly aligned graphite or "sheath" along the fiber axis. The initial

COMPOSITE NO.	CVD CARBON	PITCH	INITIAL CARB. TEMP. (°C)	GRAPH. TEMP. (°C)	PYROLYSIS PRESSURE (MPa)	FINAL DENSITY (g/cc)
P-1	NO	A240	900	2000	35.5	1.96
P-2	YES	*	*	*	*	1.93
P-3	*	15V	*	*	*	1.99
P-4	*	LS24	*	*	*	1.96
P-5	YES	LS24	*	*	*	1.94
P-6	*	*	900	*	*	1.97
P-7	*	*	1200	*	*	1.96
P-8	*	*	*	2400	*	1.98
P-9	*	*	*	2000	*	1.94
P-10	*	*	*	*	6.9	1.87**
P-11	*	*	*	*	20.7	1.96
P-12	*	*	*	*	103.4	1.94

\* SAME AS P-1

\*\* OPEN POROSITY >10%; NOT TESTED

Table 1 - Composite Summary

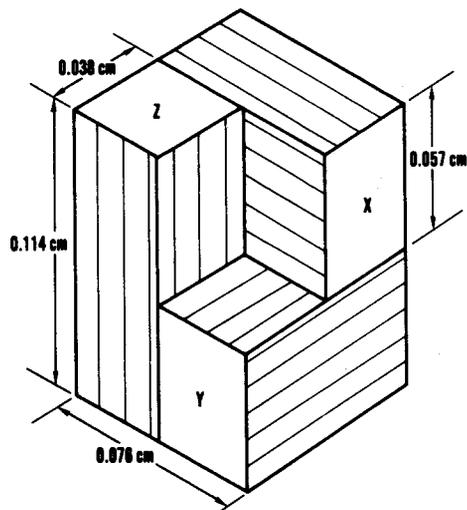


Fig. 1 - Composite Unit Cell

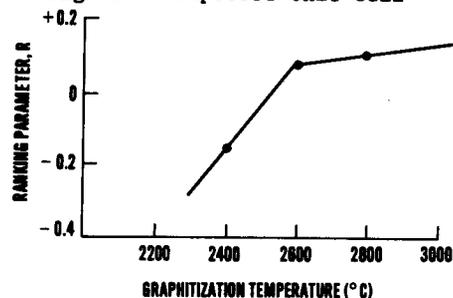


Fig. 4 - R vs Graphitization Temp.

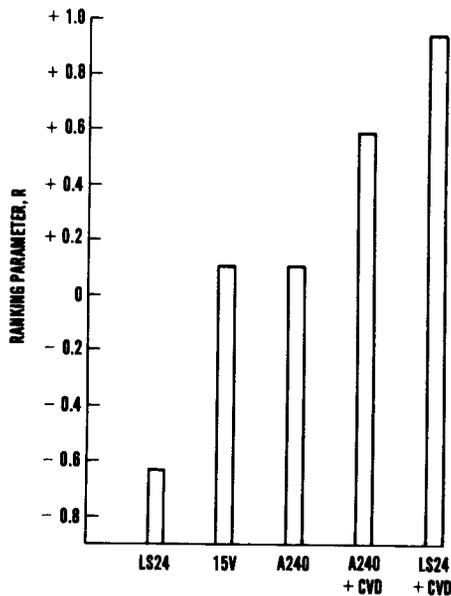


Fig. 2 - R vs Matrix Type

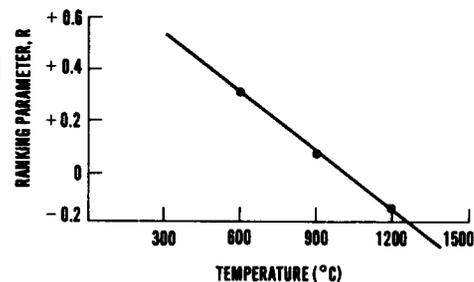


Fig. 3 - R vs Pyrolysis Temp.

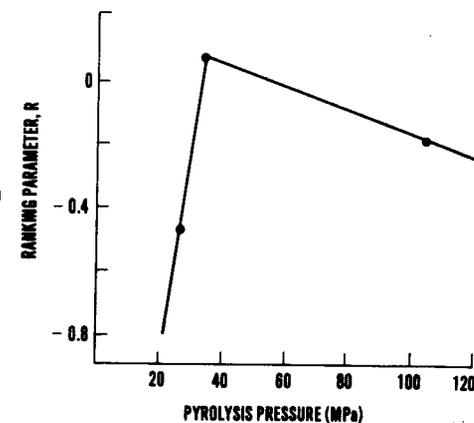


Fig. 5 - R vs Pyrolysis Pressure

carbonization temperature, although only used once during the fabrication of the composites, has a similar effect on graphite alignment: lower carbonization temperatures cause less fiber damage. For example the tensile strengths for the 600°C, 900°C and the 1200°C composites were the same ( $\pm 2\%$ ) whereas the 1200°C composite is 32% stiffer than the 600°C composite.

There appears to be a threshold graphitization temperature (2600°C) and a threshold pyrolysis pressure (34.5 MPa; 5,000 psi) above which little change in thermal stress and impact resistance is apparent. Below those thresholds there are strong adverse effects.

TEST TYPE	PROPERTY	UNITS	MINIMUM X	MAXIMUM X	$\bar{X}$	S	Cv	n
Z DIRECTION TENSILE	MODULUS	GPa	125	210	170	25	0.14	10
	STRENGTH	MPa	164	187	172	10	0.06	10
	STRAIN	%	0.86	0.15	0.11	0.02	0.17	10
Z DIRECTION COMPRESSION	MODULUS	GPa	97.2	23.4	140	34	0.23	25
	STRENGTH	MPa	66.2	62.7	66.0	7.0	0.10	25
	STRAIN	%	0.64	0.14	0.07	0.02	0.33	24
Z DIRECTION FLEXURE	MODULUS	GPa	114	102	101	22	0.14	11
	STRENGTH	MPa	197	203	178	16	0.06	11
	STRAIN	%	0.10	0.33	0.22	0.06	0.26	11
X/Y DIRECTION FLEXURE	MODULUS	GPa	26.3	120	63.2	24.0	0.30	16
	STRENGTH	MPa	36.9	117	73.1	22.2	0.30	16
	STRAIN	%	0.17	0.46	0.31	0.10	0.32	16
45° X/Y DIRECTION COMPRESSION	MODULUS	GPa	4.00	0.31	5.05	1.30	0.24	22
	STRESS AT 0.2% YIELD	MPa	0.41	26.0	14.0	4.2	0.28	22
	STRESS AT 1% YIELD	MPa	11.4	26.1	16.0	3.7	0.20	22
	STRENGTH	MPa	26.0	40.7	34.3	3.6	0.10	22

Table 2 - Mechanical Property Summary