VAPOR GROWN CARBON FIBER/PHENOLIC MATRIX COMPOSITES FOR ROCKET NOZZLES AND HEAT SHIELDS

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ABSTRACT

The ablation, mechanical and thermal properties of vapor grown carbon fiber (VGCF) (Pyrograf III™ Applied Sciences, Inc.)/phenolic resin (SC-1008, Borden Chemical, Inc.) composites were evaluated to determine the potential of using this material in solid rocket motor nozzles. Composite specimens with varying VGCF loading (30%-50% wt.) including one sample with ex-rayon carbon fiber plies were prepared and exposed to a plasma torch for 20 sec. with a heat flux of 16.5 MW/m^2 at approximately 1650°C. Low erosion rates and little char formation were observed, confirming that these materials were promising for rocket motor nozzle materials. When fiber loadings increased, mechanical properties and ablative properties improved. The VGCF composites had low thermal conductivities (approximately 0.56 W/m-°C) indicating they were good insulating materials. If a 65% fiber loading in VGCF composite can be achieved, then ablative properties are projected to be comparable to or better than the composite material currently used on the Space Shuttle Reusable Solid Rocket Motor (RSRM).

Keywords: A. Carbon fiber; B. Ablation; Thermal properties; Mechanical properties

INTRODUTION

The ablation, mechanical and thermal properties of some recently prepared vapor grown carbon fiber (VGCF) (Pyrograf III™ Applied Sciences, Inc.)/phenolic resin (SC-1008, Borden Chemical, Inc.) composites are reported herein. The purpose was to begin evaluation of this material for use in solid rocket motor nozzles and related applications.

Applied Science, Inc. (ASI) manufactures the only commercially available supply of vapor grown carbon fibers, (VGCF). The Pyrograf III™ vapor grown carbon fibers from ASI have a diameter range of between 100 - 300 nm and of lengths varying between 10 and 100 μm[1-4] The aspect ratio, l/d (length/diameter), for VGCF ranges between 100 and 1000[1]. Unlike most fibers used for composite reinforcement, VGCFs come in a fluffy mass where the fibers are curved and intertwined[1-4]. Figure 1 shows a Scanning Electron Microscope (SEM) view of a sample of Pyrograf III™ VGCF.

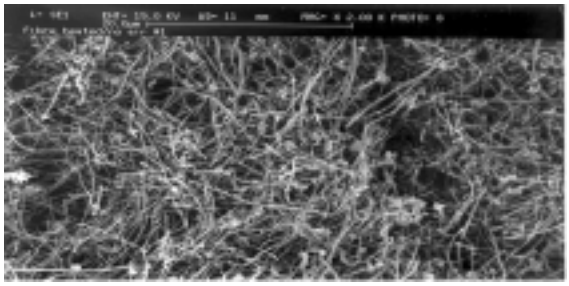

Figure 1 Scanning Electron Microscope View of Pyrograf III™ VGCF

Vapor grown carbon fibers are produced by introducing an aerosol spray of a metal salt (usually Fe^{+3}) into a chamber of hydrocarbon gas (i.e., methane or natural gas) heated to 1000 - 1200 °C [2-4]. Figure 2 depicts the production of VGCF [2].

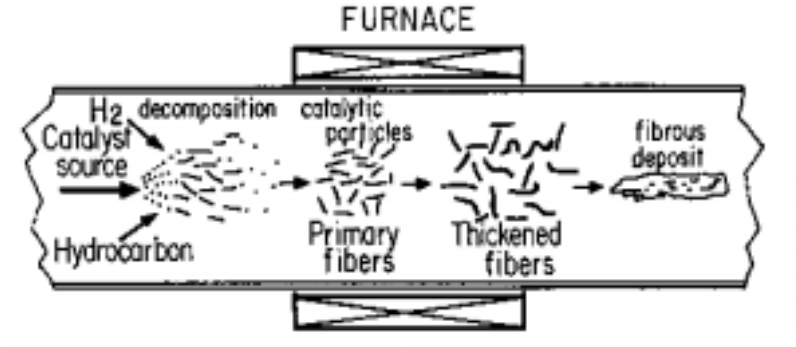

Figure 2 Three-Dimensional Growth of Fibers in a Reaction Chamber [2]

The activation of the iron particle catalyst causes the initial graphitic carbon filaments to form [2-4]. The carbon filaments may lengthen for several minutes until the catalyst deactivates [5,6]. Since the iron particle becomes the nucleation site for the fiber tip, the initial carbon fiber diameter is directly proportional to the iron particle diameter, i.e., 10 nm [2,5,7]. The filaments then lengthen and thicken further by chemical vapor deposition of carbon onto the graphitic substrate [5]. The thickening process forms concentric, cylindrical sheaths around the initial filament [2,5]. These cylindrical sheaths develop a cross-sectional tree-ring morphology [5,6]. The final filament structure has a graphitized core covered with layers of pyrolytic carbon of lower graphitization [6,7]. This tree-ring morphology is illustrated in Figure 3 [5].

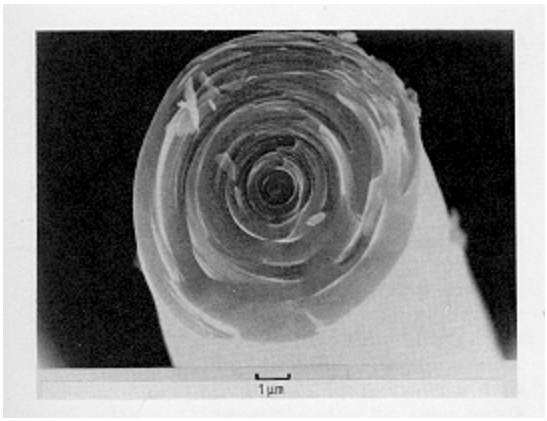

Figure 3 Transverse Section of a Vapor Grown Carbon Fiber Showing Tree Ring Morphology [5].

Vapor grown carbon fibers have two main advantages, cost and availability. VGCF can be very inexpensive due to their size and by the use of natural gas as the source of hydrocarbon gas [3,4]. Fiber diameter is a cost driver for VGCF [4]. The smaller fibers like Pyrograf III™ require less time in the reaction chamber, thus reducing cost [3,4]. Pyrograf I,™which has a fiber diameter between 1 - 100 µm (i.e., 10 to 300 times the size of Pyrograf III™), is much more expensive.

Disadvantages of Pyrograf III™ VGCFs include obtaining a non-standardized product, lack of a detailed knowledge of their material properties, and packing problems. Since Pyrograf III™ fibers are so small, the individual fiber material properties can not be readily measured [3,4,7], although Patton and Pittman have recently reported lower limits for their flexural moduli and flexural strengths [3,8]. Mechanical properties have been measured for much smaller carbon nanotubes by atomic force spectroscopy [9]. However, these techniques can not be used on Pyrograf III™ fiber, because they are too large. Pyrograf III™ material properties are assumed to be similar to Pyrograf I™ material properties, since their preparation differs only in the growth time used. However,

the ratio of pyrolytic carbon outer region to the tubular graphite inner core is different for these two classes of fibers. Table 1 lists the material properties for Pyrograf I™ fibers.

Table 1, Properties of Pyrograf I™ Fibers[a]

Property	Value	Units
Fiber Diameter	1 – 100	μm
Tensile Strength[b]	2.7	Gpa
Tensile Modulus[b]	400	Gpa
Ultimate Strain	1.5	%
Density	1.8	g/cm^3
Coefficient of Thermal Expansion	-1.0	ppm/°C
Electrical Resistance	1000	μΩ-cm
Thermal Conductivity	20	W/m-°K

[a]Source: Applied Sciences, Inc.
[b] Pyrograf III™ ranges: tensile strength 1.7-3.38 GPa, tensile modulus 88-166 GPa [8]

Mechanical properties control many applications of composites, and much VGCF composite research has focused on determining these properties [10]. Chellappa et. al. [11] Shui and Chung, [12] as well as Ciminelli et. al. [1] obtained poor mechanical properties when testing VGCF composites. Chellappa et. al. [11] attributed poor mechanical results in the VGCF composites they prepared to (1) poor fiber/matrix adhesion, (2) poor fiber dispersion, (3) the presence of voids, and (4) using a weak thermoplastic elastomer matrix having a 0.1 MPa ultimate strength. Shui and Chung [12] as well as Ciminelli et. al. [1] attributed the poor mechanical properties to insufficient bonding between the VGCF and the matrix. It is also likely that they achieved poor fiber wetting and poor fiber dispersion.

The first strength improvements in VGCF composites were observed at Mississippi State University by Patton, Pittman, and Wang. [3,4,8]. The main variable contributing to these strength improvements was the use of pre-cure high shear mixing techniques. This aided in resin infusion, which is one of the two most important problems associated with making VGCF composites. Composites with high fiber volume fractions did not have any strength improvements. These composites had poor mechanical properties due to their high porosity resulting from fiber packing problems. Packing is the second significant problem. Random three-dimensional packing of the VGCF, which have a high aspect ratio, leads to a low theoretical packing fraction. Hence, void free composites require high resin volume fractions.

The thermal properties of VGCF composites have not been as widely studied. Shui and Chung [12] showed the thermal conductivity of VGCF/polyether sulfone composites increased with fiber loading. Our group showed the thermal conductivity of VGCF composites with acrylonitrile-butadiene-styrene (ABS) and epoxy matrices increased with an increase in the fiber loading [8]. However, these increases were small. VGCF composites are not thermal conductors.

VGCF composites are being considered as a new material for the rocket nozzle of the space shuttle reusable solid rocket motor (RSRM). Currently NASA uses MX-4926, which is composed of two different reinforcements: woven ex-rayon carbon fiber from Avtex Fibers, Inc., and carbon black filler. The matrix is a phenolic matrix, SC-1008 Borden Chemical, Inc [13]. The high-temperature and high-velocity exhaust produces a pressure of 6.89 MPa and a temperature of 1650 °C in the RSRM's rocket nozzle during firing [14,15]. Not only does the rocket nozzle material have to be a good insulator, but it also must have superb ablative properties [14,15].

MANUFACTURING VAPOR GROWN CARBON FIBER/PHENOLIC COMPOSITES

VGCF/phenolic resin composite specimens were prepared by high shear mixing followed by thermal curing. Table 2 lists the 19 composite specimens made, mixing method used, their composition (wt.), density, void content, and fiber volume fraction, and the tests performed on each specimen. The VGCF/phenolic

composite specimens were tested for ablation, mechanical, and thermal properties. The cure cycles for all samples were held constant. Four types of samples were made for material testing. The compositions, expressed as wt./wt., were 30/70 VGCF/Phenolic, 40/60 VGCF/Phenolic, 40/60 VGCF/Phenolic (where ball milled as-received VGCF was used) and 45/5/50 VGCF/ex-Rayon woven cloth/Phenolic. Two types of fiber were received from ASI: as-received and compacted fiber. The compacted fiber was from a different batch than the as-received fiber, and it had been subjected to post-production compaction processing. VGCF composites made from compacted fiber had significantly higher flexure strengths than comparable samples made from as-received fiber. Compacted fiber was not used in any ablation test specimens. Due to supply problems, the compacted fiber was employed in the 45/5/50 VGCF/ex-rayon/phenolic samples, which were used in mechanical and thermal tests. These properties may differ somewhat from the baseline properties established with as-received fiber. All specimens used in ablation testing were made from as-received VGCF, so they are directly comparable.

Table 2, VGCF/Phenolic Composite Sample Properties

Sample Number	Fiber wt. (%)	Fiber Type	Sample Weight (g)	Sample Density (g/cc)	Void (%)	Fiber Volume (%)	Test Type[a]	Mixing Type[b]
1	30	As-received	16.25	1.416	1.5	20.23	M	CG
2	30	As-received	17.21	1.399	2.73	19.99	M	CG
3	30	As-received	17.87	1.396	2.95	19.94	T	CG
4	30	As-received	n/a	n/a	n/a	n/a	A	HS
5	40	As-received	18.45	1.461	3.02	27.83	M	CG
6	40	As-received	18.58	1.453	3.59	27.68	M	CG
7	40	As-received	18.29	1.462	2.95	27.85	T	CG
8	40	As-received	n/a	n/a	n/a	n/a	A	HS
9	40	Ball milled	14.99	1.484	1.42	28.27	M	HS
10	40	Ball milled	15.21	1.485	1.35	28.29	M	HS
11	40	Ball milled	14.92	1.481	1.63	28.21	T	HS
12	40	Ball milled	n/a	n/a	n/a	n/a	A	HS
13	45/5[c]	Compacted	25.53	1.477	6.04	31.7/4.3[c]	–	CG
14	45/5[c]	Compacted	26.20	1.426	9.81	30.6/4.2[c]	M	CG
15	45/5[c]	Compacted	26.62	1.426	9.81	30.6/4.2[c]	T	CG
16	45/5[c]	As-received	n/a	n/a	n/a	n/a	A	HS
17	40	Compacted	22.15	1.491	0.95	28.40	M	CG
18[d]	0	n/a	20.17	1.312	3.5	0	T	n/a
19	40	As-received	n/a	n/a	n/a	n/a	3DT	HS

[a] M=mechanical testing, T=thermal conductivity, A=ablation, 3DT=3D thermal conductivity
[b] HS=high shear sequence using Brabender and two roll mill after coffee grinder, CG=coffee ground only
[c] Ex-Rayon Carbon Fiber
[d] Pure Phenolic Sample

Ablation test specimens (specimens 4,8,12,16) were prepared as 79.4x54x35.6 mm blocks. They were cut into six specimens, which were 25.4x25.4x35.6 mm in size. Specimens 1-3, 5-7, 17 and 18 were 69.9x41.3x2.5 mm in size. Specimens 9-11 were 69.9x41.3x2.5 mm specimens and had been cut from one larger block. Similarly, specimens 13-15 were also 69.9x41.3x2.5 mm and cut from a larger block. Specimen 19 was the same size as the ablation specimens 4, 8, 12 and 16. Thermal conductivity specimens were cut from three different faces of specimen 19 in order to test for the anisotropy of thermal conductivity in these specimens.

The thermal conductivity specimens 3, 7, 11, 15 and 18 were cut into two identical 31.8x31.8x2.5 mm pieces for use in the guarded hot plate thermal conductivity test. Mechanical test specimens 1, 2, 5, 6, 9, 10, 13, 14 and 17, each of which are 69.9x41.3x2.5 mm in size, were cut into five specimens of 40x10x2.5 mm for the 3-point bending test.

1) Volume reduction

Ball milling was used to reduce the volume (increase the volume fraction) of the as-received VGCF. The ball mill consists of a cylindrical container with internal side brackets fastened to its walls, which continually lifted and dropped the balls onto the fiber. Three different ball diameters are used; 3.18 mm, 6.35 mm, and 12.7 mm; and approximately 300 balls are placed inside the ball mill. The fibers were ground in a high-speed blender before ball milling. A small amount of water was used during the grinding to aid the volume reduction. Significant volume reduction occurs after approximately 30 seconds of grinding. Then the fibers were dried at 121°C for 4 to 6 hours. Dry fibers were necessary for ball milling because excess water in the fiber cushions the impact during ball milling. The VGCF was ball milled for 16 hours. The results of this two step grinding process on VGCF are shown in Table 3. The volume reduction factors ranged between 2.94 - 11.5. The average total reduction factor was 5.34 for these samples.

Table 3, Volume Reduction of VGCF by Grinding and Ball Milling

Sample Number	Weight (g)	Original Volume (mL)	Volume After Grinding (mL)	Volume After Ball Milling (mL)	Total Factor Reduction
1	20.10	687.5	500.0	233.8	2.94
2	40.67	1437.5	887.5	300.0	4.79
3	42.31	1500.0	875.0	312.5	4.80
4	40.67	1500.0	1020.0	250.0	6.00
5	40.81	1480.0	812.5	375.0	3.95
6	40.80	1450.0	687.5	437.5	3.31
7	40.13	1500.0	625.0	250.0	6.00
8	40.24	1500.0	1000.0	312.0	4.80
9	40.24	1437.5	875.0	125.0	11.50
Average	**38.44**	**1388.1**	**809.2**	**288.4**	**5.34**

2) Mixing

VGCF/phenolic resin composites were prepared by a multi-step mixing process followed by a vacuum treatment to remove the isopropyl alcohol solvent from the phenolic resin. First, the fiber and resin were hand mixed for approximately one min. Then, the fiber/resin mixture was placed into a high speed coffee grinder and ground for 2 min. A further two step high shear mixing sequence was used when preparing the ablation test specimens 4, 8, 12 and 16 and mechanical test specimens 9-11. In the first step, the fiber/resin mixture was put into a Brabender high shear mixer at 100 rpm for 30 min. This was followed by 2-roll milling at 50° C at speeds between 50-80 rpm for 30 min. Other composite samples, used for mechanical and thermal conductivity tests, (samples 1-3, 5-7, 13-15 and 17) were not large enough for the high shear mixing in the available sized equipment. Once mixing was complete, the isopropyl alcohol was removed, *in vacuo*, at 70 mm Hg for 48 h.

3) Composite Curing

Samples were cured by heating under pressure in a mold. The mold was placed into the hot press and heated to 80°C at 5.1 MPa for 30 min. Then the temperature and pressure were increased to 104°C with 15.3 MPa for 90 min. Finally the temperature was again increased to 138°C while the pressure is held steady at 15.3 MPa for another 30 min. This allowed the water of curing to diffuse out without distorting the composite or causing voids.

TESTING PROCEDURES AND RESULTS

Density

Density measurements were made so that the percent voids and fiber volume fractions could be calculated. The void percent indirectly indicates the quality of the resin infusion. Composite density and weight measurements were made with the Electronic Densimeter Pyknometer Model # ED-120T, AFD Ltd. Density measurements were performed on the composite samples used for mechanical and thermal conductivity

measurements. The ablation test samples were too large for the densimeter's reservoir. Table 2 lists the VGCF composite samples, their fiber weight fractions, densities, percent voids, mixing regime and which tests were performed.

The void percent was less than 3% for most of the samples (Table 2) indicating relatively good resin infusion; however, the void contents in samples 13, 14, and 15 are much higher than 3%. This is probably due to delamination cracking between the ex-rayon carbon fiber layers, which occurred when specimens 13-15 were cut.

Mechanical Testing

The flexural strengths and flexural moduli were obtained from 3-point bending tests, and conducted in accordance with ASTM standard D 790M-93 using a Zwick Materials Testing Model #1435 (± 1% accuracy). A total of ten 3-point bending tests were performed for each composite type. The span was 30 mm, the width was 10 mm, and the thickness was 2.5 mm. Calculated values of the flexural strength and flexural modulus have an accuracy of ± 5%. The 3-point bending tests were performed on specimens 1, 2, 5, 6, 9, 10, 14 and 17. The results are shown in Table 4.

Table 4, VGCF/Phenolic Composite Flexural Strength and Flexural Modulus

Composite Sample #	$\%W_f$ (%)	Flex. Strength (MPa)	Flex. Modulus (GPa)
1	30	25.6 ± 1.3	1.07 ± 0.05
2	30	25.1± 1.3	0.92± 0.05
5	40	26.1 ± 1.3	1.11± 0.06
6	40	32.4 ± 1.6	1.20 ± 0.06
9	40[a]	33.2± 1.7	2.76 ± 0.14
10	40[a]	35.2± 1.8	2.21 ± 0.11
14	45/5[b]	50.7 ± 2.5	2.26 ± 0.11
17	40[b]	54.0 ± 2.7	2.69 ± 0.14

[a] Ball Milled Fiber and Extra High Shear Mixing
[b] Compacted Fiber

The flexural strengths and moduli were low for these samples. Significant modulus increases occur for the ball milled and high shear mixed samples 9 and 10, which had lower void volumes. The two specimens made with compacted fiber, sample 14 and sample 17, had higher flexural moduli and strengths. Sample 14 suffered some delamination cracking when being cut, which probably reduced its strength and modulus.

Thermal Conductivity Testing

The thermal conductivities were measured according to the ASTM C 177-85 standard test method for steady-state heat flux measurements and thermal transmission properties using a guarded-hot-plate apparatus [15]. Testing temperatures ranged between 22.2 °C and 93.3 °C. This temperature range is much lower than conditions inside the space shuttle solid rocket motor nozzle. A specimen size was 31.8x31.8x2.5 mm was used.

Table 5 displays the measured thermal conductivities. All of the composite samples exhibited similar thermal conductivities (.54 to .62 W/m--°C). These values were only about twice that of the cured phenolic resin without fiber (.28 W/m-°C).

Table 5, VGCF/Phenolic Composite Thermal Conductivities

Composite Sample #	Fiber wt. (%)	Thermal Conductivity (W/m-°C)
18	0	0.28 ± 0.07
3	30	0.57 ± 0.02
7	40	0.54 ± 0.01
11	40[a]	0.62 ± 0.01
15	45/5[b]	0.57 ± 0.03

[a] Ball Milled Fiber and Extra High Shear Mixing
[b] Compacted Fiber

The thermal conductivities in three dimensions were obtained on a 40/60 VGCF/phenolic ablation test composite sample (sample 19, Table 2). Specimens were cut out of the top, side and front of the ablation test specimen. The results are shown in Table 6. They indicate that the material is roughly isotropic, differing by less than ± 9.1% from the average in all 3 directions.

Table 6, Three-Dimensional Thermal Conductivity Testing

40/60 VGCF/Phenolic Specimen Orientation	Thermal Conductivity (W/m-°C)	Percent Difference (%)
Top	0.7788 ± 0.0374	-----
Side 1	0.8275 ± 0.0407	6.25
Side 2	0.7080 ± 0.0276	9.09

Ablation Testing

Thiokol, Inc performed all ablation testing at the NASA Marshall Space Flight Center. A Plasma Torch Test Bed was used for ablation testing. This test simulates the firing conditions of the Reusable Solid Rocket Motor (RSRM), with the exception of the 6.89 MPa pressure produced inside the RSRM rocket nozzle. The plasma torch has a standoff distance of 25.4 mm and uses an argon/nitrogen mixture. A heat flux of 16.47 MW/m^2 is produced at a plasma temperature of 1649 °C. The ablation test has a 20-second burn time. Before each test began, the sample was preloaded with a 444.82 N force, called the starting load. At the end of the burn, the final load was measured. The final load was greater than the starting load due to restrained thermal expansion. Six tests were completed for each composition and the results were averaged (Table 7).

Table 7, NASA/MSFC Plasma Torch Ablation Test Results[a]

Composite Sample	Erosion Rate μm/sec (mils/sec)	% Weight Change (%)	Load Change N (lb)
30/70 VGCF/PH	1.372 ± 0.203 (0.0543 ± 0.0076)	7.7 ± 0.14	668.7 ± 82.3 (150.3 ± 18.5)
40/60 VGCF/PH	1.245 ± 0.203 (0.0487 ± 0.0076)	8.6 ± 0.19	771.0 ± 76.6 (173.3 ± 17.2)
40/60 VGCF/PH[b]	1.689 ± 0.157 (0.0665 ±0.0062)	9.37 ± 0.30	614.6 ± 107.6 (138.2 ± 24.2)
45/5/50 VGCF/Ex-Rayon/PH	1.278 ± 0.229 (0.0503 ± 0.009)	8.76 ± 0.21	635.3 ± 53.3 (142.8 ± 12.0)
MX-4926	0.787 ± 0.080 (0.031 ± 0.0034)	10.4 ± 0.21	1952.8 ± 281.2 (439.0 ± 63.2)

[a] Plasma torch test temperature 1649°C and heat flux 16.5 MW/m^2.
[b] Ball Milled Fiber

Ablation behavior was characterized by three parameters in the plasma torch test: erosion rates, specimen percent weight change, and the increase in load. NASA's standard nozzle material, MX-4926, was tested along with the VGCF composites. The MX-4926 composite is composed of woven ex-rayon carbon fiber, carbon black

filler and a phenolic matrix. The MX-4926 has a larger total carbon loading, with 65% of the composite weight constituting either carbon fiber or filler.

As compared to the MX-4926 baseline, the VGCF composites experienced: 1) higher (58-114%) erosion rates, 2) lower weight losses (10-26%), and 3) lower load changes (60.5-68.5%). Thus, the VGCF specimens had less char and heat penetration than MX-4926. Therefore, more weight was being lost at or near the surface of the specimen versus weight loss from subsurface thermal decomposition. The load did not change much with increasing VGCF content (30%-50% wt.). Furthermore, the load changes for the VGCF composites are significantly lower than that of the MX-4926 composite. Load change is an indirect measure of heat penetration and char depth. Increases in load change indicate an increase in heat penetration and char depth. The VGCF composites appear to be far better insulators than the MX-4926. The higher erosion rates of the VGCF samples probably reflect their lower carbon content. The VGCF samples had a significantly lower carbon loading (30-50%) than the MX-4926 composite (65%).

Qualitative Observations of Ablation

Several interesting observations were made of the ablative action of these specimens.

1) There was no bright spot where the torch impinged on the specimen. The heat appeared to be spread uniformly across the surface, indicating good in-plane thermal conductivity.
2) The ablation proceeded with a flaking action. Very thin, small flakes of heated material would peel off from the specimen. This flaking action was uniform across the specimen for the higher carbon loading specimens (>30% wt.).

Because the load change was low during these ablation tests, the heat penetration, and hence out-of-plane thermal conductivity, was low. Thus, in ablative conditions, the specimens appeared to have higher in-plane than out-of-plane thermal conductivity. This apparently contradicts the results for room temperature thermal conductivity, which were nearly isotropic. A possible mechanism to explain this would be the formation of VGCF/carbon matrix (with high thermal conductivity) flakes on the surface, followed by flaking. This is speculative; much further work needs to be done in this area.

CONCLUSIONS

VGCF/phenolic composites, prepared with extensive high shear mixing, should be made with higher carbon loadings (50%-65% wt.) and subjected to the plasma torch tests. They have exhibited good erosion resistance at low carbon loadings while exhibiting less weight loss and load change than the material currently used on the RSRM.

The plasma torch testing indicates that this class of composites is a good candidate for future development for rocket nozzles and heat shielding materials. This is particularly true since both the VGCF manufacturing and processing technology is in its infancy. The carbon loadings used in VGCF composites so far have been much lower than that used in the MX-4926 composite. Much further work needs to be done at higher carbon loadings.

The mechanical properties of the VGCF composites need improvement. Lower void volumes, better surface treatments for fiber/matrix adhesion and mixed VGCF/carbon fiber weaves/carbon filler combinations should be investigated. VGCF/phenolic composites are virtually unstudied and should be the target of future efforts.

The VGCF/phenolic composites have a low thermal conductivity, and that they have roughly equal conductivity in all directions. This might imply that the fiber alignment is 3-D random, or if a higher order alignment exists in microregions, such microregions are randomly oriented within the macroscopic sample.

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