SINTERED CARBON VAPOR GROWN CARBON FIBER COMPOSITES

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Introduction

Vapor grown carbon fibers (VGCF) offer a unique opportunity for carbon fiber composites to expand into a multitude of new markets due to their low cost of only $1-3/lb. Additionally, VGCF's are extremely graphitic and have demonstrated the highest thermal conductivity of any graphite material. Pyrograf-III®, a VGCF produced by Applied Sciences, Inc., is a small diameter fiber with a high aspect ratio used in this study. The primary interest of the work is for thermal management applications with carbon-carbon(C-C) composites. The work has focused on developing novel process methods for these unusual fibers using pitch, phenolic and epoxy matrices to produce low cost composites.

The VGCF's do not look like conventional carbon fibers. They are typically 0.1 - 0.5 μm in diameter and are 100 to 500 hundred μm in length with a density of 2.0 g/cc. They are produced in a semi-continuous process from methane gas. The batchlike fluffy mass of intertwined VGCF's is very different from a standard fiber tow. It has a bulk density of only 0.29 kg/m³. VGCF's exhibit a circular orientation of the graphitic planes through the cross section of the fiber versus the radial arrangement found in conventional carbon fibers [1]. Theoretical work shows that the high aspect ratio should produce composites with properties approaching those of continuous fibers [2]. VGCFs are extremely graphitic and should produce highly conductive composites. C-C composites with a thermal conductivity of near 1000 w/m-k have been produced using another variation of VGCF [3-4].

The size and form of the VGCFs fibers is very different from that of conventional carbon fibers. Because of this, compounding fibers and resin for composites is very different from methods used for conventional carbon fibers such as hand lay-up of prepreg and filament winding. Methods that have been considered include: vacuum infiltrating a fiber mat with resin, mechanical mixing, slurry processing, milling, and hot pressing.

Other processing steps include carbonization, and graphitization. Finally, as composites have been fabricated, tests to determine processing success include mechanical strength and stiffness, electrical resistance, and micro structural examination.

Experimental

The matrix was Mitsubishi AR mesophase pitch. It was jet milled to an average particle size of 1.5 μm and stabilized in air and then jet milled again. A mechanical mixing process was used to distribute the VGCFs into a particle/solvent system with a drill powered mixing blade. The solvent/resin system provides a medium to wet the fibers and allow for high shearing of the system which produces a homogenous mixture. Solvents included water with a surfactant, Lubrizol 240, or acetone. Mixing times varied from 5 to 150 minutes depending on speed, blade type, and material components. This distributed mixture is then dried to remove solvents. Once the pitch and fibers were evenly mixed and the solvents removed, the pitch matrix samples were crumbled into particles of approximately 2-5 mm and evenly distributed into a steel mold. These samples were pressed at 5 - 45 ksi and 75 - 300 °C for 30 - 60 minutes. The pitch matrix composites were produced based on a sintering study by Hill [5]. From that work three points with the best processing characteristics and the highest flexural strength values were selected as the starting point to process VGCF's with pitch.

Figure 1. Sintered VGCF Composite

The carbon-carbon composites created by the aforementioned process were then carbonized and graphitized in the following manner. The carbonization furnace was heated at a 1 - 2°C per minute ramp up to a temperature of 1000°C, held for four hours, then followed by a slow cool down. All steps were conducted in a flowing nitrogen gas environment. Graphitization was performed in a graphite induction furnace for a sample size up to 3" by 3". Graphitization is not complete.

Results and Discussion

The pitch matrix composites were evaluated primarily with the measurement of flexural strength, thermal conductivity, and electrical resistivity. Other data included flexural stiffness, tensile strength and stiffness, density, SEM, weight loss, dimensional change, and observation. Many of the key properties are summarized in Table 1.

The bulk density of the composites peeked at 1.57 g/cc, while the apparent densities ranged from 1.6 - 1.9 g/cc. The zeros for the crack and bloat values indicate that no cracking or bloating occurred during the carbonization cycle. The composites showed very little warpage and survived processing extremely well. All of the strength and modulus properties tended to decrease with increasing fiber volume. Conversely, the electrical resistance improved (decreased) with fiber volume up to 40 %. The best composite produced to this point was sample C2B. This sample had a 25% raw pitch content in the matrix. The thermal conductivity values centered around 2 W/mK. Although these are not highly conductive values, there are several factors which may indicate that the composites may be useful. The data shown is for carbonized composites heat treated to approximately 900° C. They also contain only 20 fiber by weight. With higher fiber loading and full heat treatment, these composites could have conductivities of 200 - 400 W/mK. Additionally, the through-thickness conductivities are relatively high and should improve proportionally with the in-plane values.

Conclusions

The C-C composites using the mechanical mixing process showed good repeatability, process survivability, and offer the most promising properties. With further heat treatment (graphitization) these composites should be cost competitive with other thermal management materials.

Table 1. Sintered VGCF Composite Results

ID	Fiber Dens %	Fiber Dens g/cc	Tensile Str psi	Tensile Mod msi	Flexural Str psi	Flexural Mod msi	Elect Resist mOhm-cm	Ther Cond X-Y W/mK	Ther Cond Z W/mK
B2	0	1.48	n/a	n/a	4142	n/a	39.19		
B2A	20	1.31	2610	1.84	3343	1.58	30.82	2.28	1.30
B2B	30	1.17	1799	1.14	2085	1.06	23.77	1.82	0.93
B2C	40	1.27	1911	1.30	1937	1.03	24.42		
B2D	60	0.54	n/a	n/a	n/a	n/a	85.02		
B2E	30	0.99	601	1.55	2140	n/a	17.21		
B2F	50	0.82	n/a	n/a	n/a	n/a	76.75		
C2	0	1.57	n/a	n/a	8136	2.43	30.41		
C2A	20	1.21	565	0.90	1712	1.02	27.33	1.65	1.10
C2B	20	1.28	4204	2.40	6932	0.00	16.09	2.71	1.53
C2C	25	1.14	2195	1.58	3790	0.00	21.53		
C5	0	1.43	n/a	n/a	6895	1.47	23.77		
C5A	20	n/a	n/a	n/a	n/a	n/a	68.45		
C5B	33	0.69	n/a	n/a	n/a	n/a	84.37		

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