

VAPOR GROWN CARBON FIBER COMPOSITES WITH EPOXY AND POLY(PHENYLENE SULFIDE) MATRICES

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Introduction

Vapor grown carbon fibers (Pyrograf III from Applied Sciences, Inc.) with 0.1 - 0.3 diameters and ~10 to 100 μm lengths were formulated into epoxy (thermoset) and into poly(phenylene sulfide) (thermoplastic) composites with various fiber volume fractions. Increases in stiffness were observed as with previous VGCF/organic matrix composites. Large increases in flexural strengths were achieved in both systems demonstrating that discontinuous randomly oriented Pyrograf III has substantial potential as a reinforcement in composites. These may be the first strength increases observed for VGCF/epoxy matrix composites. Here-to-fore, addition of VGCF caused strength decreases. Voids, residual thermal strains (given the fiber surface area is ~35 times greater than 7 μm -diameter PAN fiber), or uncertainties about fiber strength, fiber-matrix bonding and the degree of fiber dispersion could cause losses of strength.

Pyrograf III occupies 270 cm^3/g until it has been preground/mixed with resin. Surface tension, viscosity and boundary layer problems lead to difficulties in (1) getting resin infused throughout the fiber (2), coating a high fraction of fiber surface and (3) removal of air. The volume contraction during epoxy curing and the mismatch in resin vs fiber thermal expansion coefficients may affect VGCF composites differently than conventional CF composites (large fiber surface area effect?). Therefore, we studied higher shear mixing, pressing under vacuum, and low temperature curing to study epoxy matrix composites.

Experimental

A low viscosity, epoxy resin/aliphatic amine hardener from Clearstream Products, Inc. (9000) and Shell's EPON 830 (100 parts), m-phenylenediamine (11.5 parts), methylene dianiline (7.5 parts) diluted in acetone (180 parts) were employed. Both unground and wet ground (ball milled 15h) Pyrograf III (dried 24 h at 120°C) were used. Resins and Pyrograf III were preblended at various weight ratios (5/95 to 50/50) in a blender (3000 rpm). Selected samples were subjected to ~2h of continual repetitive passes through a two roll mill (0.2 mm gap) to effect high shear mixing. After precuring 6-8h at 23°C the fiber/resin mass was press cured in an Al mold under various conditions (pressure/vacuum etc.). All samples were postcured either at 22-25°C for one week or at 120°C for 4h to complete the cure.

Poly(phenylene sulfide), PPS, from Phillips 66 (Ryton P-6) was a fine powder. Pyrograf III was blended (3000 rpm) with Ryton P-6 for 30 to 120 s. The mixture was pressed at 300 atm, heated at 320°C for 2.5h and quickly molded on a preheated (120°C) press at 300-600 atm. (20 min.). Composites with V_f of 3.3 to 49.5% were made. Untreated and oxygen-plasma treated (200 W, 15 min. at 0.2 torr) fibers were used.

Results

Epoxy composites. When fibers and low viscosity epoxy resin were only mixed in the blender (not the two roll mill) and press-cured at 1000 psi at 23-24°C the flexural moduli of the resulting composites increased continuously with the fiber volume fraction (V_f) (Table 1). The flexural strength initially increased as V_f increased to 15-17% and then began to fall. The void content increased gradually (to a fiber $V_f = 20\%$) then rapidly (to 9.3% voids) at $V_f = 35.5\%$. Holding V_f at 15.5% different curing conditions were compared: (a) 8h precured at 1 atm, 21°C, then under 1000 psi at 49°C, 8h; (b) 8h precure *in vacuo* (0.08 atm) at 21°F, then press-cure under 1000/250 psi press release cycles at 49°C, 8h; (c) precured *in vacuo* (0.08 atm) at 21°F and then press-cure at 1000 psi and 127°C for 1h, 20 min. Locked in press-induced fiber strains were studied by comparing (a) with (b). Entries 7-9 of Table 1 (versus entree 3) show that curing at 49°C gave a greater strengths than curing at 21 or 127°C. The 127°C cure lowered the strength (residual thermal strain?). Vacuum press curing (eg. b) to assist resin infusion and air removal didn't effect the void volume or flexural strength.

Two roll mixing, after blender mixing, subjected the fiber-epoxy mixture to higher shear and led to higher flexural strengths. Strength increases of 45.5 and 67.9% over pure resin were obtained at $V_f = 15.5$ and 19.2%, respectively (see Table 2). Curing protocols (a-c above) showed that: (1) vacuum curing offered no advantage; (2) 127°C cures lowered composite strengths vs. 49°C cures.

The EPON 830 epoxy system was mixed with fibers using acetone (solvent). The resin was precured (16h) then press-cured at 127°C (1h, 20 min.) at different pressures and post cured at 1 atm. at 100°C (2h) and 150°C (2h). Vacuum press-curing offered no advantage. Applying 250 or 500 psi pressures during pressing gave a large strength improvement (33-34%) vs. curing at ambient pressure (3% strength improvement) due to a large reduction in voids. Neither

Table 1. Properties of Unground Pyrograf III/Low Viscosity Epoxy Resin Composites Prepared By Blender, Mixing. Effect of Fiber V_f and Curing Conditions

Fiber Vol. Fraction V_f (%)	Void Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Strength Improvement (%)
0 ^a	-----	2.29	87	-----
2.82 ^a	0	2.40	93.2	6.9
15.5 ^a	1.24	5.98	104.8	20.2
19.2 ^a	1.79	6.24	95.9	10.0
27.9 ^a	2.65	7.18	88.5	1.5
35.5 ^a	9.33	8.74	70.9	-18.7
15.5 ^b	1.61	6.18	112.5	29.0
15.5 ^c	1.61	6.36	112.0	28.4
15.5 ^d	1.47	6.57	103.2	18.3

^a Press-cured at 1000 psi at 21°C for 16h at 1 atm.

^b Precured 8h at 21°C then press-cured at 1000 psi at 49°C, 8h.

^c Precured 8h at 21°C at 0.08 atm, then press-cured under 1000/250 psi press-release cycles at 0.08 atm. at 49°C, 8h.

^d Precured 8h at 21°C at 0.08 atm, then press-cured at 1000 psi at 127°C for 1h, 20 min.

grinding or O₂ plasma treatment of the fibers increased composite strength or modulus at $V_f = 15.5\%$.

The Pyrograf III fiber modulus was approximated from the measured flexural moduli using $E_c = KE_f V_f + E_m (1 - V_f)$, where K is the reinforcing efficiency (3-D random 0.2, 2-D random 0.375)¹. The data in Table 2: $V_f = 15.5\%$, composite flexural modulus = 6.85 GPa and resin flexural modulus = 2.29 GPa leads to a Pyrograf III modulus between 88 to 166 GPa. Pyrograf III appears to be highly random in 3D (SEM or composites and fibers), so $K \approx 0.2$. Thus, a modulus of 150-166 GPa is suggested. Fiber strengths were crudely estimated employing¹ $\sigma_{\mu c} = K(1 - \ell/2\ell)\sigma_f V_f + (1 - V_f)\sigma_m$. Our measured data was used assuming $\ell = 2\ell_c$ and $K = 0.2$ to 0.375. A fiber flexural strength range from ~5.1 to 2.55 GPa resulted (estimated tensile strength range is 3.38 - 1.70 GPa assuming flex strength is 50% greater).

Poly(phenylene sulfide), PPS, composites. Composites made with (a) untreated (b) wet ground and (c) O₂ plasma-treated fibers exhibited increasing flexural strengths (3 point bending) as the fiber V_f increased (Table 3). Then strengths decreased as the V_f further increased (Table 3). Void volumes increase rapidly at V_f values above 30%. Strength enhancements of 91% above that of pure PPS resulted when wet ground fibers were used at $V_f = 21.2\%$ (3.3% voids). A 66% enhancement occurred using plasma-treated fibers ($V_f = 21.3\%$, (2.8% voids).

Infusion of viscous (melt flow index = 650g/10 min., 5 kg, 316°C), high melting (285°C) PPS into pyrograf was very difficult during the preheat (320°C, no applied pressure) or hot pressing (120°C, high pressure) giving higher voids than low viscosity epoxy resins gave. High shear mixing (> 285°C) would likely give better composite properties.²

Table 2. Properties Versus Curing Conditions of Unground Pyrograf III/Low Viscosity Epoxy Matrix Composites Prepared Using a Blender and Two Roll Mill Mixing

Fiber Vol. Fraction (%) (Press Cond.)	Void Content (%)	Flexural Modulus (GPa) ^b	Flexural Strength (MPa) ^b	Strength Improvement ^b (%)
15.5 (1)	1.22	6.85	126.9	45.5
15.5 (2)	1.38	6.47	124.2	42.4
15.5 (3)	2.18	6.43	113.0	29.6
19.2 (1)	1.90	7.02	146.4	67.9

^a Conditions 1, 2 and 3 are given in footnotes b, c and d, respectively, of Table 1.

^b The pure epoxy resin exhibited a flexural modulus of 2.29 GPa, and flexural strength of 87 MPa.

Table 3. Flexural Strengths^a of Pyrograf III/Poly(phenylene sulfide) Composites Versus Fiber Volume Fraction (V_f).

V_f (%)	O ₂ Plasma-Treated Fiber Composites			Wet Ground Fiber Composites		
	Void Vol (%)	Flexural Strength (MPa)	Strength Improvement (%)	Void Vol. (%)	Flexural Strength (MPa)	Strength Improvement (%)
0	-----	70	-----	-----	70	-----
3.3	0.3	71	1	0.5	68	-3
6.7	1.0	77	10	1.1	69	-1
13.8	1.9	98	40	1.9	96	37
21.3	2.8	116	66	3.3	134	91
28.6	5.4	106	51	5.8	93	33
31-34 ^b	13.4	77	10	21.3	54	-23
33-37	32.5	33	-53	24.7	57	-19

^a 3 Point bending results on 6.4 cm³, 2.85 cm. dia. samples

^b $V_f = 34\%$ for O₂ plasma-treated and 31% for wet ground fibers

References

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2. *Handbook of Composites*, ed. G. Lubin, Van Nostrand Reinhold, New York, 1982, p. 250.