

An experimental study of carbon-carbon composite materials

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A systematic exploratory development study of the mechanical behaviour of pyrolyzed organic resin matrices reinforced with high performance carbonaceous fibres was performed. Fourteen combinations of fibre and precursor matrices in unidirectional composite form were fabricated and tested. Physical, thermal, and mechanical properties were determined at various process stages. A principal conclusion was that it is the very poor interfacial bond which is typically achieved between fibres and matrix that accounts for the low mechanical properties which are commonly observed. This poor bond was attributed primarily to the mismatch between the transverse thermal expansion coefficient of the graphite fibres and the thermal expansion coefficient of the surrounding matrix. Among the recommendations made is that the carbonization/graphitization conditions be modified to promote better interfacial bonding.

1. Introduction

Carbon-carbon composite materials, i.e. graphitized carbon matrices reinforced with high performance carbonaceous fibres, are strong candidates for use in high temperature applications. Carbon-carbon composites offer several advantages over currently employed materials such as bulk graphite and ceramics – specifically with respect to mechanical properties and resistance to thermal shock damage.

The development of currently available carbon-carbon composites has included only a few detailed characterizations of the effect of the constituent materials and process variables on the composite thermal and mechanical properties [1, 2]. The present study represents another step in the development of a basic understanding of the phenomenology controlling the behaviour of carbon-carbon systems. This development is identifying areas in which specific improvements are needed, and is suggesting approaches to effect these improvements.

The present investigation is related specifically to pyrolyzed organic resin matrix systems. That

is, a graphite-fibre-reinforced organic resin matrix material is first fabricated and cured (polymerized) in essentially the same manner as is a standard polymer-matrix composite. The matrix in this composite is then carbonized by heating the composite. Since the polymer matrix materials in current use typically produce a carbon yield of only 60 to 65% by volume after the noncarbon volatiles are evolved, the resulting as-carbonized composite is very porous. A high composite density is desired as it characteristically results in better ablation characteristics and higher mechanical properties.

To reduce this porosity, the composite is subjected to several additional process cycles, during which it is successively reimpregnated with a low viscosity resin, cured, and recarbonized, thereby successively increasing its density. The composite is then heated to and held at a temperature of 5000°F (~2760°C) or higher in an inert atmosphere for several hours or more, resulting in a thermally stable form. In principle this process converts the amorphous carbon matrix to a graphitic crystalline structure; in actual practice an only partially ordered struc-

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ture is typically obtained [3].

However, because of the difference in coefficients of thermal expansion between the highly oriented crystalline structure of the graphite fibres and the turbostratic structure of the matrix, thermal residual stresses are induced in the composite during cooldown from the 5000°F graphitization temperature. In particular, the cross-sectional dimensions of the fibres contract more than the surrounding matrix material. The relatively weak bond, if any, between fibre and matrix is readily broken, and a gap is formed at the fibre-matrix interface. This results in an "opening-up" of the composite as it is sometimes called, and an increase in apparent porosity. Typically, the composite is cycled through three or more of these full reimpregnation-cure-carbonization processes, or until the incremental increase in density no longer justifies the additional processing effort.

2. Description of materials

A total of fourteen different fibre-matrix combinations were evaluated. Three different precursor matrices and six different carbonaceous fibres were utilized, representing a wide range of both physical and mechanical property variations.

2.1. Matrix constituents

Three resin systems were employed as precursor matrices:

(a) Monsanto's SC-1008 resin is a conventional phenolic for which processing and pyrolyzation characteristics were known. It was utilized in a 60% solids solution in isopropanol.

(b) Polyphenylquinoxaline (PPQ) resin, pioneered and supplied by the United States Naval Ordnance Laboratory, offered potentially high carbon yields and possibly improved thermomechanical properties.

(c) Ironside's FF-26 high solids phenolic resin was selected for evaluation because it offered a low weight loss during cure and a potentially high carbon yield, as compared to conventional phenolic resins.

For the purpose of densifying the carbon-carbon composites, two reimpregnating resin systems were employed. The principal reimpregnate was a furfuryl type resin (Quaker Oats' P-3) which had the required low viscosity and was an excellent carbon former. However, furfuryl resins exhibit a high exotherm during cure and the composite, being very porous initially, picks up a considerable amount of reimpregnating resin. Also, its quite low viscosity presents a resin retention problem in the early stages of densification. For these reasons, a modified furfuryl system was employed in the early reimpregnation stages. This system, referred to as ENF, was a mixture of epoxy novalac (Dow's DEN 438) and P-3 furfuryl, which exhibited a higher viscosity and less exothermic reaction.

2.2. Fibre constituents

A total of six carbonaceous fibres were included in the programme, and are briefly described in Table I. A wide range of variables was represented. Moduli ranged from 16×10^6 to 76×10^6 psi, strengths from 165×10^3 to 425×10^3 psi, and densities from 1.31 to 1.86 g cm^{-3} . Both tow

TABLE I Properties of reinforcement fibres (manufacturers' data)

	Fibre					
	Thornel 75S	Modmor I	HMG 50	Thornel 16	Thornel 50S	Thornel 400
Manufacturer	Union Carbide	Morganite	Hitco	Union Carbide	Union Carbide	Union Carbide
Form	Yarn	Tow	Yarn	Yarn	Yarn	Yarn
Filaments per bundle	720	10 000	720	480	720	1000
Filament diameter (μm)	6.0	7.8	7.5	8.0	6.6	7.6
Carbon assay (%)	99.9	*	99.9	99.9	99.9	92.0
Density (g cm^{-3})	1.82	1.86	1.72	1.31	1.67	1.78
Strand breaking strength (10^3 psi)	360	250	290	165	320	425
Strand modulus (10^6 psi†)	76	56	50	16	57	32
Strand elongation (%)	0.5	*	*	1.0	0.5	1.3

*Data not available.

† 10^3 psi = 6.89 N mm^{-2} .

and yarn forms, both rayon and polyacrylonitrile precursor fibres, and three different manufacturers were represented. Probably a more important variable was the range of prior processing temperatures, which was estimated to be from 2000°F (~ 1088°C) (Thornel 400) to greater than 5000°F (Thornel 75S). All fibres were utilized in their as-received condition.

3. Carbonization cycle determination

In order to establish carbonization heat cycles for the carbon-carbon processing, thermal gravimetric analyses (TGA) and differential thermal analyses (DTA) were performed for the several resin systems involved. The apparatus utilized was a Robert L. Stone Model 12A, with a heat rise of 7°F min⁻¹ (~ 4°C min⁻¹) in a nitrogen flow. The analyses were conducted to 1830°F (~ 999°C). TGA and DTA curves were obtained for both reinforced and unreinforced precursor resins, and for reinforced reimpregnating resins. The thermal analysis tests were made on both the reinforced and unreinforced matrix systems in order to determine if a similar response to the thermal environment was obtained. The reinforced samples contained approximately 50% by volume of Union Carbide Corporation graphite fibres (WYB 85-1/2) for the SC-1008 precursor matrix and the P-3 and ENF reimpregnation resins, and Thornel 50S for the PPQ and FF-26 precursor matrices). The unreinforced precursor resin castings were prepared at atmospheric pressure, employing lengthy dwell times at several temperatures. Final cure temperature conditions were as follows:

SC-1008: 18 h at 350°F (~ 177°C)
 PPQ: 5 h at 300°F (~ 149°C)
 FF-26: 21 h at 280°F (~ 138°C)

The TGA curves for the precursor resins were more informative than the DTA curves, and typical examples are illustrated in Fig. 1. In addition to providing information for the subsequent carbonization temperature profile, these thermal analyses showed the following: (a) the same general trend was observed for reinforced and unreinforced samples; (b) reactions were exothermic; (c) weight losses corresponded approximately to those reported in the literature.

From a detailed evaluation of both TGA and DTA curves, for both unreinforced and

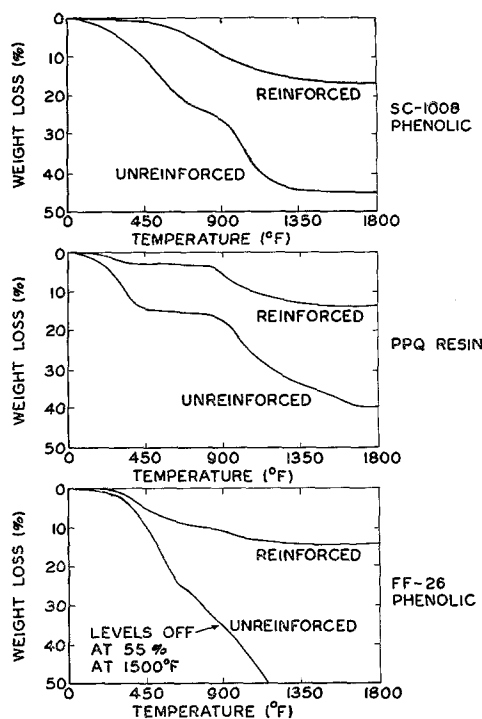


Figure 1 Thermal gravimetric analysis curves for reinforced and unreinforced precursor matrices.

reinforced resin systems, it was concluded that a common carbonization heat cycle would be suitable for all of the various carbon-carbon systems, since exothermic/endothermic reactions and weight loss inflection points occurred in approximately the same temperature regions. This cycle was as follows:

(a) Place materials in a steel retort and pack with coke breeze.

(b) With a continuous flow of nitrogen, heat the materials in a cam-controlled cycle room temperature to 550°F (~ 288°C) in 10½ h, 550 to 750°F (288 to 439°C) in 16 h, 750 to 1400°F (439 to 760°C) in 7½ h.

Carbon yields were obtained with each resin system, employing the carbonization cycle to be used with the carbon-carbon composites. The carbon yield results are shown in Table II. Yields of greater than 60% by weight were demonstrated for PPQ, FF-26 and P-3 furfuryl reimpregnating resin. Note that these results are in the same general range as obtained with TGA, but that there was some variation, particularly for FF-26 phenolic. This suggests that the actual

TABLE II Properties of organic resins utilized

	Resin				
	SC-1008 Phenolic	PPQ	FF-26 Phenolic	ENF, Novalac/ Furfuryl Blend	P-3 Furfuryl
Manufacturer	Monsanto	Naval Ordnance Laboratory	Ironsides	Dow/Quaker Oats	Quaker Oats
Use	Precursor matrix	Precursor matrix	Precursor matrix	Reimpregnating resin	Reimpregnating resin
Carbon yield* (% by weight)	49.6	62.3	66.4	55.6	61.8
Density† (g cm ⁻³)					
as-cured	1.22	1.18	1.30	1.27	1.23
carbonized	1.39	1.38	1.37	1.38	1.43
graphitized (one cycle)	1.47	1.47	1.44	1.46	1.46
graphitized (2 cycles)	—	—	—	—	1.52
graphitized (3 cycles)	—	—	—	—	1.56

*Carbonized to 1400°F under same cycle as employed for carbon/carbon composites.

†Pycnometer densities of finely ground samples.

carbonizing process conditions should be used to determine carbon yields for candidate matrices.

Densities after carbonization and graphitization were obtained for the five resins involved. Standard pycnometer methods were employed with finely ground samples (cyclohexane was the displacement liquid). The densities are also listed in Table II. Since the P-3 furfuryl was to be the major matrix former in the carbon-carbon composites, densities were obtained through three graphitization cycles. Note that the densities after first graphitization for all five resin systems were quite similar. The density of the furfuryl system continued to increase with successive graphitization cycles, to a value of 1.56 g cm⁻³.

4. Composite fabrication process

Unidirectional laminates (5 × 7 in.) were fabricated using fourteen combinations of fibres and precursor resins. All fibres were impregnated with resin on a drum winder to form collimated composite sheets. A controlled amount of precursor resin was uniformly dispersed into the fibres. The target thickness was 0.08 in. and an estimated number of plies were laid up unidirectionally to yield this thickness. The number of plies varied from six for Thornel 16 to as many as 18 for Thornel 75S laminates. The fibre volume was controlled by applying a known amount of resin to a known weight of fibres. The

target of 60% fibres by volume was attained in most cases. However, the Thornel 50S/SC-1008 and Modmor I/PPQ laminates exhibited a fibre volume of less than 50%.

Some difficulty was experienced in processing the initial PPQ matrix laminates with a press type cure. Subsequent PPQ laminates were fabricated using an autoclave process. Thus, the possible effect of precursor processing variables should be kept in mind when the composite test results for PPQ are considered.

Carbonization, reimpregnation and graphitization procedures were as follows:

- carbonize to 1400°F (as described in Section 3)
- impregnate with ENF and recarbonize (three times)
- graphitize to 5000°F
- impregnate with P-3 furfuryl and recarbonize (three times)
- graphitize to 5000°F
- impregnate with P-3 furfuryl and recarbonize (three times)
- graphitize to 5000°F.

Thornel 400 laminates were not graphitized, but were exposed to all nine densification cycles to the carbonizing temperature of 1400°F.

5. Physical properties of carbon-carbon composites

Individual density measurements were made for

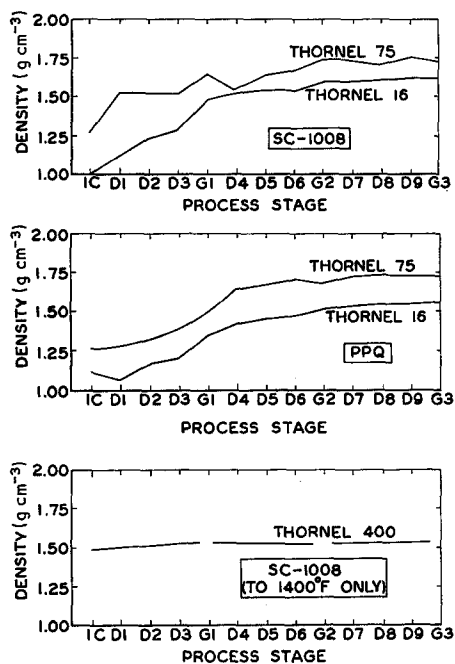


Figure 2 Density versus process stage for typical carbon-carbon composites.

each carbon-carbon system after each process stage. Fig. 2 illustrates the typical response of the carbon-carbon composites to continued densification cycles. In viewing these curves, it should be remembered that the volume shrinkage influenced the values obtained. The general trend was for a levelling off after the second graphitization. To establish the final composite densities, measurements were made on six additional samples of each system after the third and final graphitization. Relatively high densities were attained in most cases. Dimensions of the density samples were also recorded for the purpose of studying dimensional changes during the processing.

The typical trends observed for the graphitized carbon-carbon were:

(a) the major portion of the volume decrease of all systems occurred during the first graphitization cycle;

(b) the major portion of the volume decrease was attributable to transverse shrinkage (normal to the fibres);

(c) longitudinal dimensional changes (parallel to the fibres) were minor;

(d) SC-1008 precursor panels shrank less than those of the other two precursor matrices.

Determination of carbon-carbon fibre volume and void content after final processing developed

into a major task. The planned method comprised the following steps:

(a) Photomicrographic count of yarn or tow bundles from a polished sample (density of sample determined prior to count).

(b) Calculation of fibre bundle cross-sectional area from measured density and measured weight per unit length.

(c) Calculation of fibre volume from total fibre bundle area and area of micrograph counted.

(d) Calculation of void content from difference between theoretical density (based on calculated fibre volume) and actual sample density.

In order to reliably count the fibre bundles in a carbon-carbon sample, some experimentation with polishing and photomicrography techniques was necessary.

Calculation of bundle cross-sectional area required the measurement of density and weight per unit length. It was decided that these measurements should be performed on fibres which had been subjected to similar conditions as the carbon-carbon. The result was the discovery that definite changes in density occur to the carbonaceous fibres when exposed to the graphitizing cycles employed in this programme.

Density was determined for various fibres in the as-received condition and after one, two or three graphitization cycles. Verification of these measurements was accomplished by employing three distinct methods, described as follows:

(a) Pycnometer with trichloroethylene as the displacement liquid, with bell jar evacuation.

(b) A float/sink method with benzene and tetrabromoethane, determining the density of the blended liquids with a pycnometer.

(c) Specific gravity by displacement in distilled water after bell jar evacuation.

A definite increase in density occurred in the five cases tested, and the increase appeared to progress with successive graphitization cycles. The density increase ranged up to 27% (Thornel 50S).

Typical fibre volumes and void contents obtained by the methods indicated are listed in Table III. The calculated densities were obtained using the measured fibre density and P-3 furfuryl density, both after three graphitizations. The density of the reimpregnating resin P-3 was used because P-3 was common to all composites, representing approximately 50% of the final matrix, and the scope of the programme did not allow determination of the density of each precursor resin through three

TABLE III Fibre volume and void content of selected carbon/carbon systems after final processing

Precursor matrix	Fibre	Fibre volume ¹ (%)	Calculated density ² (g cm ⁻³)	Actual sample density (g cm ⁻³)	Calculated void content ³ (%)
SC-1008	Thornel 75	64	1.83	1.71	7.6
	Modmor I	71	1.86	1.75	6.9
	Thornel 16	72	1.65	1.61	2.3
	Thornel 50	46	1.74	1.54	13.1
PPQ	Thornel 75	70	1.86	1.69	10.5
	Modmor I	57	1.75	1.70	6.4
	Thornel 16	76	1.65	1.51	9.1
	Thornel 50	79	1.89	1.71	10.6
FF-26	Thornel 75	73	1.87	1.77	6.2
	Thornel 50	72	1.85	1.74	6.9

Notes: ¹Fibre volume determined by photomicrograph count of fibre yarns or tows.

²Density calculated using fibre and reimpregnating matrix densities determined after three graphitization cycles, assuming no voids.

³Void content calculated as the difference between calculated and actual densities of the photomicrographed sample, expressed as percent of matrix density (per ASTM Standard D-2734).



Figure 3 SEM of diamond saw cut carbon-carbon composite cross-section (Thornel 75S/FF-26 after third graphitization), $\times 5200$.

graphitizations. Since the data are based on a small area of one sample per system, the fibre volumes and void contents should be considered as indicative. However, the fibre volumes demonstrated the increase from those of the as-cured panels due to shrinkage, and the void contents indicated a relatively low final porosity for many of the carbon-carbon systems.

Scanning electron microscopy (SEM) was used to further characterize the physical aspects of the carbon-carbon composites. Fig. 3 is an SEM

view of a diamond saw cut edge which illustrates several phenomena, in particular the fact that the matrix appears to be stratified or layered. The layers are believed to represent successive depositions from reimpregnating/carbonizing cycles. Since the layers appear to separate easily from each other, there undoubtedly is a bonding problem between matrix layers as well as to the fibres.

6. Mechanical properties of carbon-carbon composites

Mechanical test specimens were cut from the carbon-carbon composites after each of five different process stages (except for the non-graphitized Thornel 400 panels for which specimens were taken after four process stages), three specimens per condition. Longitudinal and transverse tensile properties, flexural properties, and shear strengths were determined.

The mechanical test results are summarized in Tables IV, V, and VI. It should be noted that the bulk densities tabulated in the last columns represent average values, whereas the values given in Table III are for specific specimens.

6.1. Longitudinal tensile properties

Good longitudinal tensile strengths and moduli (properties in the direction of fibre reinforcement) were reached by many of the fibre/precursor matrix combinations as densification increased, although not as high as would be expected with organic matrices. Panels reinforced with Thornel 75S, Thornel 50S and Modmor I fibres exhibited the higher strengths and moduli.

TABLE IV Summary of average mechanical properties of SC-1008 precursor matrix composites after various process stages

Fibre	Process stage	Longitudinal tensile properties				Transverse tensile properties				Flexural properties					
		Strength (psi)	Modulus (10 ⁸ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁸ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁸ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁸ psi)	Short beam shear strength (psi)	Bulk density (g cm ⁻³)	
Thornel 75	1st Carb.	69 700	46.3	0.12	180							26 700	34.6	3700	1.26
	3rd Dens.	71 800	52.7	0.13	820							89 800	46.1	2700	1.52
	1st Graph.	92 000	55.4	0.17	630							87 700	48.1	3100	1.65
	2nd Graph.	101 000	56.8	0.19	580	0.57	0.11					81 700	48.2	3200	1.74
	3rd Graph.	118 500	53.2	> 0.18	680	0.42	0.19					86 300	49.1	3600	1.74
Madmor I	1st Carb.	34 200	31.1	0.10	65							30 600	18.4	1000	1.42
	3rd Dens.	54 400	31.9	0.17	270							47 300	27.0	3100	1.64
	1st Graph.	74 700	41.1	0.18	380							29 100	30.2	3100	1.75
	2nd Graph.	82 900	43.0	0.19	290	0.82	0.05					59 600	34.5	2500	1.82
	3rd Graph.	83 900	39.9	0.22	620	0.42	0.19					55 600	33.1	2900	1.83
VMG-50	1st Carb.	16 500	21.6	0.07	70							34 400	22.1	900	1.22
	3rd Dens.	37 300	30.1	0.13	170							78 400	24.5	3600	1.47
	1st Graph.	51 700	35.3	0.13	230							70 300	24.5	2100	1.60
	2nd Graph.	50 200	34.7	0.16	310	0.28	0.12					63 600	33.3	4000	1.70
	3rd Graph.	48 500	37.3	0.13	580	0.43	0.16					67 200	30.2	2400	1.72
Thornel 16	1st Carb.	4 900	9.4	0.02	20							12 700	7.1	440	0.99
	3rd Dens.	28 800	10.0	0.34	120							41 100	9.5	1600	1.29
	1st Graph.	30 100	13.1	0.24	240							53 800	12.5	2300	1.46
	2nd Graph.	45 500	14.6	0.32	280	0.88	0.04					61 800	14.3	2700	1.60
	3rd Graph.	41 800	13.7	0.31	640	0.61	0.14					45 000	13.5	2700	1.61
Thornel 50	1st Carb.	36 400	31.8	0.12	45							62 800	33.3	3100	1.31
	3rd Dens.	30 400	30.8	0.11	570	0.75	0.10					50 200	36.3	3600	1.37
	1st Graph.	76 900	38.9	0.20	270	0.57	0.06					46 300	25.4	2200	1.44
	2nd Graph.	69 500	38.9	0.18	580	0.47	0.14					52 800	26.8	2900	1.50
3rd Graph.	80 700	40.6	0.20	730	0.55	0.15					59 800	33.0	3300	1.50	
Thornel 400	1st Carb.	12 700	21.0	0.08	390	0.44	0.05					22 500	20.0	3200	1.49
	3rd Dens.	11 100	20.5	0.05	500							21 800	18.9	2200	1.52
	6th Dens.	4 200	16.5	0.02	870	1.29	0.07					15 800	18.5	1100	1.51
	9th Dens.	8 300	14.5	0.05	830	2.11	0.05					11 700	17.4	1100	1.52

TABLE V Summary of average mechanical properties of PPQ precursor matrix composites after various process stages

Fibre	Process stage	Longitudinal tensile properties					Transverse tensile properties					Flexural properties				
		Strength (psi)	Modulus (10 ⁶ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁶ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁶ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁶ psi)	Short beam shear strength (psi)	Bulk density (g cm ⁻³)		
Thornel 75	1st Carb.	31 300	40.3	0.08	96	0.16	0.09	34 300	30.3			1600	1.27			
	3rd Dens.	22 300	27.2	0.08	300	0.73		35 700	31.8			2100	1.38			
	1st Graph.	61 400	43.2	0.14	350	0.29	0.18	43 400	32.7			1800	1.50			
	2nd Graph.				370	0.39	0.11	46 800	35.7			2100	1.68			
	3rd Graph.	72 900	42.1	0.17	380	0.21	0.19	49 800	39.9			2300	1.72			
Modmor I	1st Carb.	17 300	14.8	0.10				21 000	17.0			800	1.19			
	3rd Dens.	20 300	25.5	0.07	160	0.23	0.06	24 400	21.5			1700	1.39			
	1st Graph.	51 100	29.1	0.19	220	0.19	0.14	41 700	26.0			2600	1.54			
	2nd Graph.	41 700	32.4	0.14	340	0.27	0.15	44 300	25.7			1900	1.72			
	3rd Graph.	64 400	35.8	0.17	480	0.46	0.18	45 200	28.8			2700	1.78			
Thornel 16	1st Carb.	8 100	3.9	0.28	14			6 900	4.2			220	0.90			
	3rd Dens.	33 000	7.8	0.59	140	0.28	0.10	57 500	7.6			2200	1.21			
	1st Graph.	33 700	10.4	0.32	410	0.43	0.12	62 300	10.3			2100	1.35			
	2nd Graph.	25 100	11.3	0.24	400	0.45	0.11	67 400	11.1			2000	1.52			
	3rd Graph.	37 900	12.3	0.32	450	0.62	0.08	57 700	10.7			2400	1.55			
Thornel 50	1st Carb.	9 900	22.5	0.05				16 500	19.7			1200	1.20			
	3rd Dens.	21 500	30.2	0.08	190	0.18	0.10	29 200	28.4			2400	1.37			
	1st Graph.	47 600	25.0	0.20	340	0.34	0.21	45 400	19.7			2700	1.58			
	2nd Graph.	52 200	36.1	0.15	470	0.27	0.12	70 900	33.3			3300	1.72			
	3rd Graph.	40 700	37.0	0.12	380	0.34	0.15	87 500	27.7			4100	1.74			
Thornel 400	1st Carb.				90			24 400	17.0			1300	1.29			
	3rd Dens.	10 800	20.4	0.10	670	0.73	0.11	19 000	18.7			1300	1.44			
	6th Dens.	9 300	15.4	0.06	680	0.96	0.07	15 200	19.6			1500	1.45			
	9th Dens.	15 600	18.2	0.09	630	0.84	0.08	12 300	16.5			2100	1.45			

TABLE VI Summary of average mechanical properties of FF-26 precursor matrix composites after various process stages

Fibre	Process stage	Longitudinal tensile properties				Transverse tensile properties				Flexural properties		
		Strength (psi)	Modulus (10 ⁶ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁶ psi)	Strain to failure (%)	Strength (psi)	Modulus (10 ⁶ psi)	Strength (psi)	Modulus (10 ⁶ psi)	Short beam shear strength (psi)
Thornel 75	1st Carb.	58 600	44.5	0.13	160	0.15	0.08	51 400	45.0	1600	1.50	
	3rd Dens.	46 600	45.6	0.10	530	0.88	0.06	55 500	46.5	2700	1.58	
	1st Graph.	83 400	46.2	0.19	330	0.19	0.19	57 600	41.4	2500	1.75	
	2nd Graph.	108 400	54.0	0.20	320	0.36	0.10	39 700	46.1	1800	1.78	
	3rd Graph.	108 600	56.8	0.19	760	0.46	0.18	61 100	53.7	1600	1.78	
Thornel 50	1st Carb.	30 600	25.6	0.12				47 200	21.9	2600	1.38	
	3rd Dens.	26 200	28.7	0.09	420	0.74	0.05	42 500	25.3	2400	1.48	
	1st Graph.	91 200	39.2	0.24	450	0.46	0.10	77 300	37.9	3600	1.64	
	2nd Graph.	77 000	40.0	0.19	170	0.16	0.13	67 900	35.6	3800	1.68	
	3rd Graph.	81 500	41.3	0.20	400	0.42	0.07	90 900	39.6	3800	1.70	
Thornel 400	1st Carb.	26 500	17.1	0.15	84			31 400	16.9	1900	1.43	
	3rd Dens.	18 300	19.7	0.09	100	0.13	0.05	30 600	16.6	2600	1.55	
	6th Dens.	21 700	18.7	0.12	390	0.62	0.05	24 300	17.6	2400	1.53	
	9th Dens.	16 200	18.8	0.08	760	1.29	0.07	21 800	16.3	2300	1.55	

Note that Thornel 400 fibre reinforced carbon-carbon composites decreased in both strength and modulus as the carbonizing process continued. Strain-to-failure was relatively low and approximately equivalent for all systems, except that the Thornel 16 reinforced panels yielded slightly greater strain values. The trend as regards densification was that strength steadily increased from somewhat low levels after the first carbonization, whereas modulus generally reached most of its final value early in the processing. Typical variations of tensile and flexural strength versus process stage are graphically illustrated in Fig. 4. Scanning electron microscopy revealed that fibre pullout of moderate extent generally occurred (except in the case of Thornel 400, for which fibre pullout was much less noticeable).

6.2. Transverse tensile properties

Transverse tensile specimens were fragile, particularly in the early densification cycles. The use of an extensometer was not attempted for many of the specimens in the first stages of processing. In the later part of the programme a special extensometer was obtained which weighed only about $\frac{1}{2}$ oz. (15 g) and was a significant benefit in obtaining stress/strain curves.

Transverse tensile properties (properties normal to the direction of fibre reinforcement) were uniformly low, being in the neighbourhood of a few hundred psi strength and less than 10^6 psi modulus. Strain to failure values were low and comparable to those obtained for longitudinal specimens. No significant difference was noted among the various fibres and precursor matrices. The general trend was for a definite increase in transverse strength as densification increased. An anomaly in the data was that Thornel 400 specimens, which steadily degraded in all other properties, exhibited the greatest final transverse strengths and a marked increase in modulus in the later process stages.

6.3. Longitudinal flexural properties

Longitudinal flexural specimens (fibres parallel to the beam axis) were tested under two-point loading with a span:depth ratio of 35:1. The distance between loading points was one-half that of the support span, with $\frac{1}{4}$ in. radius load and support points being used.

In the majority of cases, the flexural strengths and moduli reached most of their maximum value by at least the first graphitization stage, as

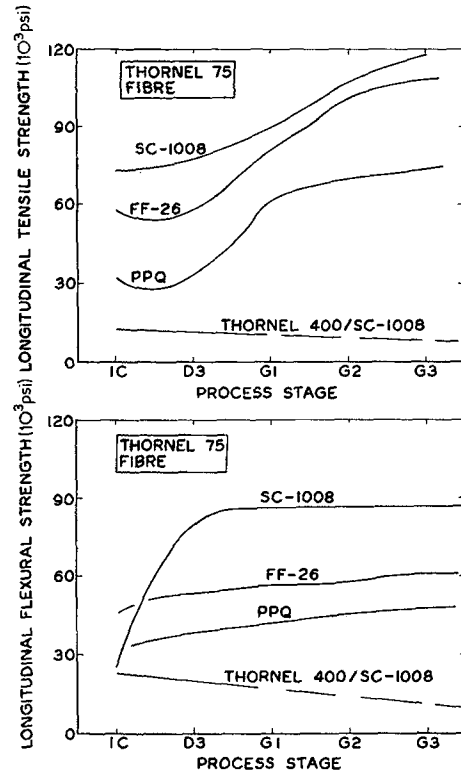


Figure 4 Longitudinal strength versus process stage for carbon-carbon composites.

shown in Tables IV, V and VI. Again, Thornel 400 fibre reinforced composite properties degraded as processing continued.

A comparison of the flexural properties obtained with the three precursor matrices indicates that, contrary to the trends observed with longitudinal tensile data, no definite precursor matrix effect is noticeable with the flexural strengths, although the SC-1008 precursor matrix composite specimens possessed greater moduli.

6.4. Short beam shear strength

The short beam shear test is a single-point loading flexure test, with a low span:depth ratio to promote shear failure. The testing was conducted with $\frac{1}{8}$ in. radius load and support points and a nominal span:depth ratio of 5:1. As summarized in Tables IV, V and VI, the short beam shear strengths did not indicate any significant trends, other than the degradation trend of Thornel 400 composites. Shear strengths of some systems approached reasonable values, but densification generally did not appear to

increase the strength level.

Failures were principally in interlaminar shear, with some compression failures at the first carbonization stage. Thornel 400 specimens failed in tension, snapping into two pieces, in the same manner as the Thornel 400 flexural specimens.

7. Thermal properties of carbon-carbon

The coefficient of thermal expansion to 1100°F (~593°C) was obtained in the longitudinal and transverse directions (parallel and normal to the direction of fibre reinforcement, respectively). A Leitz dilatometer was employed with a temperature rise of 18°F min⁻¹ (~10°C min⁻¹). The longitudinal thermal coefficient for the higher modulus fibre specimens was near zero, generally slightly negative, regardless of precursor matrix. The transverse thermal coefficient for the higher modulus fibre specimens was substantially greater, near 56×10^{-7} in. in.⁻¹F⁻¹. The Thornel 400 carbon-carbon composites behaved differently, with longitudinal coefficients being positive and in the neighbourhood of 4×10^{-7} in. in.⁻¹F⁻¹. The coefficients of thermal expansion did not appear to be influenced by the carbonization/graphitization processing.

As an additional point of information, one sample of graphitized (one cycle) P-3 furfuryl matrix (unreinforced) was tested for thermal expansion. The measured coefficient was 19×10^{-7} in. in.⁻¹F⁻¹.

8. Discussion

The present investigation has demonstrated that carbon-carbon unidirectional composites consisting of a pyrolyzed organic matrix reinforced with high performance carbonaceous fibres can be processed to high densities with good longitudinal mechanical properties. However, improvement is needed in transverse tensile and shear properties, which are thought to be low at present due to the low interfacial bond strength achieved between the fibres and the matrix.

Of the fourteen matrix/fibre combinations evaluated, the combination of the Monsanto SC-1008 phenolic precursor resin matrix and the Union Carbide Thornel 75S graphite fibres consistently exhibited higher mechanical strength properties in the longitudinal direction than any other combination.

It is possible that a higher carbonization temperature might have resulted in improved mechanical properties in general since, at 1400°F

a significant amount of volatiles were retained, which might have disrupted the material during the subsequent graphitization process. It is suggested that in future work a 2800°F carbonization temperature be utilized, which will ensure the volatilization of most of the non-carbon impurities. This higher carbonization temperature will also perform another important function; it will result in a larger ribbon-like gap being formed around each fibre during the subsequent cool-down. Since such a gap will be formed anyway during the graphitization cycle, this will offer the opportunity to increase the rate of densification (by reimpregnating to fill this gap during successive carbonizations). In this way the final gap remaining after graphitization will be considerably smaller than that existing in the composites of the present investigation.

In this regard it is further suggested that only one graphitization cycle be utilized. In the present investigation, the multiple graphitizations were used to "open-up" the composite structure. If a higher carbonization temperature is used, there will be almost no volatiles remaining to be removed, and the ribbon-like gap will have already been reduced in size by reimpregnation. The use of a single graphitization cycle will possibly offer the additional advantage of producing a matrix which is more homogeneous, and possibly it will also promote improved bonding between matrix layers.

Acknowledgements

This investigation was conducted under the sponsorship of the REVMAT Program at the United States Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, under the technical direction of C. R. Rowe and F. J. Koubek. The authors wish to thank Messrs Rowe and Koubek for their guidance and valuable suggestions. They also wish to acknowledge the extensive assistance of their colleagues, R. L. Miller and J. L. Kirkhart of Aeronutronic, and A. K. Miller of the University of Wyoming.

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Received 25 March and accepted 7 June 1974