Material and Process Effects on Carbon/Carbon Composite Shear Strength

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Extensive evaluations have been conducted to determine the effect of material and processing variables on the shear strength of carbon/carbon composites. Characteristically, the interlaminar shear strength of these materials is relatively lower than the other mechanical properties, such as cross ply shear, tensile, compression, flexure, and bearing strength. Shear strength data were obtained for various carbonaceous matrices and processing histories. These data are evaluated in relation to effects on both high- and low-modulus graphite fabric reinforced systems. Results indicate that chemical vapor deposition (CVD) and/or combinations of CVD and resin/pitch matrix presursors are methods for achieving higher interlaminar shear strength in carbon/carbon composites, and unidirectional fabrics are best for high cross ply shear strengths.

THE use of a carbon/carbon composite material in advanced solid rocket motor nozzle components depends, to a large extend, on the shear strength of that material. Variations in fabric weave and ply orientation in order to utilize cross ply shear properties are alternatives available to the designer. However, in general, interlaminar shear becomes the critical or limiting property for almost all components fabricated as carbon/carbon composites. Cross ply shear can be tailored by selection of type of reinforcement and type of weave. On the other hand, the possible variation of interlaminar shear strength is quite limited, without utilization of three-dimensional weaves. Use of a three-dimensional weave requires a tradeoff study, because a reduction of other mechanical properties, and often an increase in component price, results. All of the carbon/carbon composite materials evaluated for shear strength were laminated two-dimensional weaves. Included in the evaluation were variables of fabric type as well as matrix material.

The potential for high tensile strength and modulus of carbon/carbon composites through the use of high modulus fibers has been demonstrated.[1] However, a need for improvement in the interlaminar shear strength was indicated. The shear properties discussed in this paper provide a basis for further improvement and better predictability of shear strength in carbon/carbon composites.

Although many of the combinations of fabric weaves and yarns discussed below had not been developed prior to the evaluation program, the program was not specifically a materials development program, but rather a screening program. Furthermore, the data collected and contained herein are not from a statistically planned program to compare variables systematically and establish a cause/effect relationship. However, a sufficiently large sampling of materials and processes was made to allow analysis for trends and to draw conclusions as to what matrices and reinforcements produce the best shear strength.

II. Shear Strength of Carbon/Carbon Composites

Although carbon/carbon materials are still in the development stage, the available combinations of reinforcement, weaves, and matrices are almost infinite. For discussion, the materials evaluated are divided into three basic matrix material systems. These are 1) resin/pitch, 2) resin/pitch/chemical vapor deposition (CVD), and 3) CVD. The CVD includes "source" comparisons with several reinforcements. Evaluations also are made of reinforcements and weaves with the matrix held constant. The warp and fill thread count, as well as the precursor, are given for each of the materials evaluated.

Fiber volumes greater than 50% generally are not satisfactory for processing into CVD matrices. Therefore, the comparison of CVD and resin/pitch matrices (approximately 60% fiber volume) are somewhat misleading. However, the production process limitations make the comparison valid for actual production of carbon/carbon composites. A summary of the data used in the analysis and subsequent discussion is shown in Table 1. The materials 1-20 are described as to fabric, matrix, weave of fabric, and fiber volume in Tables 2 and 3.

All of the interlaminar shear test data were obtained by loading a notched specimen (Fig. 1) in compression. the specimen is very similar to the Federal Test Method Standard (FTMS) 406 specimen which is loaded in tension. All failures occurred between plies as indicated by the dotted line in Fig. 1. The test specimens were ground to dimension. The critical dimensions for the specimen are 1) depth of notch and 2) parallel ends. The ends were parallel within ±0.002 in., and the notch depth was a minimum of 0.006 in. past the specimen centerline for each specimen. The side supports depicted in Fig. 1 are to prevent bending of the specimen. No pressure is applied on the sides; however, a close fit is required similar to the type A, method 1042, FTMS 406.

The cross ply shear specimen is the FTMS 406, method 1041. This was used for both ambient and elevated temperature testing. Cross ply induces the shear plane across the fabric for either warp or fill direction, which is converse to the between ply shear plane for the interlaminar shear specimen just discussed.

A. Resin/Pitch Matrices

It is difficult to categorize carbon/carbon composites because of the infinite variation possible in fabrication. However, the general classification of resin/pitch matrices applies to the following type of fabrication sequence: 1) impregnation of a fabric or tape with phenolic resins, 2) layup to configuration followed by a cure/pressure polymerization cycle for the resin, 3) pyrolization and graphitization of matrix material in an inert atmosphere up to temperature of 5000°F, 4) densification by impregnation with a "pitch" or pitch/resin combination, and 5) graphitization of the "pitch" matrix. The general characteristic of the resin/pitch matrices is the dimensional change (shrinking) of the matrix, which occurs each time a cured resin/pitch matrix is pyrolized. Therefore, the dimensional stability of a part depends on the

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Table 1 Summary of shear strength values for carbon/carbon composites

Material designation[a]	Type matrix	Direction of load in relation to fabric	Ultimate shear strength, psi	Test temperature, °F
1.0	Resin/pitch	Warp	1368	RT
			2400	5000
		Fill	609	RT
			1455	3000
		45°[b]	696	RT –
		Cross ply (warp)	7250	RT
		Cross ply (fill)	3475	RT
2.0	CVD	Warp	2346	RT
		Warp	3933	4000
		Fill	1071	RT
		Cross ply (warp)	7733	RT
3.0	CVD	Warp	2820	RT
		Warp	5200	4000
		Fill	1780	RT
		Cross ply (warp)	8066	RT
4.0	CVD	Warp	1860	RT
		Fill	1190	RT
5.0	CVD	Warp	NA	RT
		Fill	NA	RT
6.0	Resin/pitch	Warp	735	RT
		Warp	1781	4000
		Cross ply (warp	5876	RT
		Fill	808	RT
		Fill	1740	4000
7.0	Resin/pitch	Warp	810	RT
		Fill	330	RT
		Cross ply (warp	6066	RT
8.0	CVD	Warp	533	RT
		Cross ply (warp)	13513	RT
9.0	CVD	Warp	1833	RT
		Fill	1385	RT
		Cross ply (warp)	16870	RT
10.0	CVD	Warp	1200	RT
11.0	CVD	Warp	1953	RT
		Cross ply (warp)		
12.0	CVD	Warp	2880	RT
13.0	Resin/pitch	Warp	656	RT
		Cross ply (warp	6933	RT
14.0	Resin/pitch	Warp	713	RT
		Warp	2050	4000
		Cross ply (warp)	5266	RT
		Fill	540	RT
		Fill	1455	4000
15.0	Resin/pitch	Warp	1862	RT
		Fill	1190	RT
16.0	Resin/pitch	Warp	715	RT
		Fill	435	RT
		Cross ply (warp)	6166	RT
		Cross ply (fill)	2033	RT
17.0	Resin/pitch	Warp	625	RT
		Fill	455	RT
		Cross ply (warp)	7166	RT
18.0	CVD	Warp	1266	RT
19.0	Resin/pitch	Warp	1578	RT
		Fill	1780	RT
		Cross ply (warp)	2500	RT
20.0	Resin/pitch	Warp	1800	RT
		Fill	1450	RT
		Cross ply (warp)	2500	RT

[a]See Table 2 for material description by fabric and matrix. See Table 3 for description of fabric warp and fill warns and variables in matrix by material supplier.
[b]45° bias to warp and fill.

machanisms of both shrinking and coalescing. Naturally, those systems which delaminate cannot be considered in the evaluation, although, adjacent to the delaminated area, high shear strengths are obtainable.

In Fig. 2, a comparison of 10 materials made by the resin/pitch process just outlined is shown. For six of these materials, (6, 7, 13, 14, 16, and 17) from polyacrylonitrile (PAN) precursor, the shear strengths are basically the same, approximately 700 psi. Material No. 7 contains a unidirectional fabric, and the shear strength is less than 400 psi in the fill direction because of the low fiber percentage (approximately 10%) in the fill direction. The approximate fiber volume for each fabric, warp to fill, is shown in Table 3. The same pattern of lower shear strength in the fill direction also is found for all other materials with lower fill volume than warp volume. Conversely, No. 6 contains a bidirectional fabric, and the shear strength is the same in both the warp and fill directions.

The causes for the higher shear strength of the four materials (Nos. 1, 15, 19, and 20) shown in Fig. 2 are not

Table 2 Material identification by number for fabric and matrix combinations

Material identification	Fabric[a]	Resin	Impregnant[b]	CVD matrix
1	5451	A	XX	...
2	5451	...	...	HCVD1
3	5451	...	...	CVD1
4	5451	...	...	HCVD2
5	5451	...	...	CVD2
6	3131	A	X	...
7	3831	A	X	...
8	3831	...	...	HCVD2
9	3831	...	...	HCVD1
10	7100	...	...	HCVD2
11	7100	...	...	HCVD1
12	7100	...	...	CVD1
13	7100	A	X	CVD1
14	7100/WCA	A	X	...
15	7431	B	XX	...
16	6331	A	X	...
17	6331	C	YYY	...
18	6331	C	YY	CVD2
19	WCA	A	X	...
20	WCA	B	YYY	...

[a]See Table 3 for fabric and matrix description. [b]The single letter indicates one impregnation, two letters two impregnations, etc.

Table 3 Reinforcement and matrix description and designation code

Fabric number	Warp yarn	Fill yarn	Vol. ratio	Weave
5451	T-50S	T-50S	4/1	8HS
3131	3000-filament panprecursor	3000-filament pan precursor	1/1	8HS
3831	T-300 3000-filament	T-300 1000-filament	11/1	5HS
7100	GY-70	None	100	None
7431	GY-70	T-300	4/1	Plain
6331	HMS	T-300	3/1	Plain
6331	HMS	T-300	3/1	5HS
WCA	Rayon precursor	Rayon precursor	1/1	Plain

Matrix	Source	Condition
CVD1	Supplier No. 1	As-deposited
HCVD1	Supplier No. 1	Heat-treated to 4500°F
CVD2	Supplier No. 2	As-deposited
HCVD2	Supplier No. 2	Heat-treated to 4500°F
Resin A	Resins are from three	Graphitized 4500°F
Resin B	sources generally	Graphitized 4500°F
Resin C	described by the suppliers as high carbon yielding phenolic "type" resins	Graphitized 4500°F
Impregnant X	Resin/pitch-proprietary	Graphitized 4500°F
Impregnant Y	Resin/pitch-proprietary	Graphitized 4500°F

readily apparent. However, some trends are indicated. Three of the four are from rayon precursors. Materials Nos. 1, 15, and 20 had two or more impregnations. Although multiple impregnations do not always provide a high shear strength, shear strengths generally are improved by additional impregnation. For example, material No. 17 received three impregnations of pitch/resin, and the shear strength was not significantly better than material 16 (a similar fabric), which had only one impregnation. However, the resin/pitch system used for impregnation was different, as shown in Table 3. Other factors which could contribute to the higher shear strengths of materials 1 and 15 are 1) lower fabric thickness (0.010 or less), 2) type and source of precursor, and 3) surface treatment and/or shape of the graphite filaments. Although direct comparisons were not made, it appears that higher shear strengths are obtained from rayon precursors and thinner fabrics.

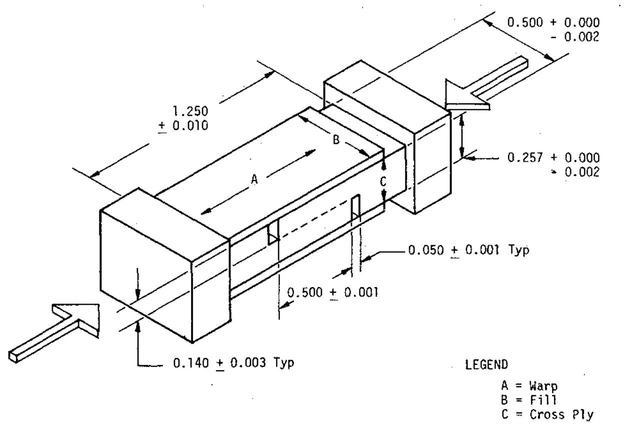


Fig. 1 A warp compression interlaminar shear specimen with end plates and side supports. Legend: A = warp, B = fill, C = cross ply.

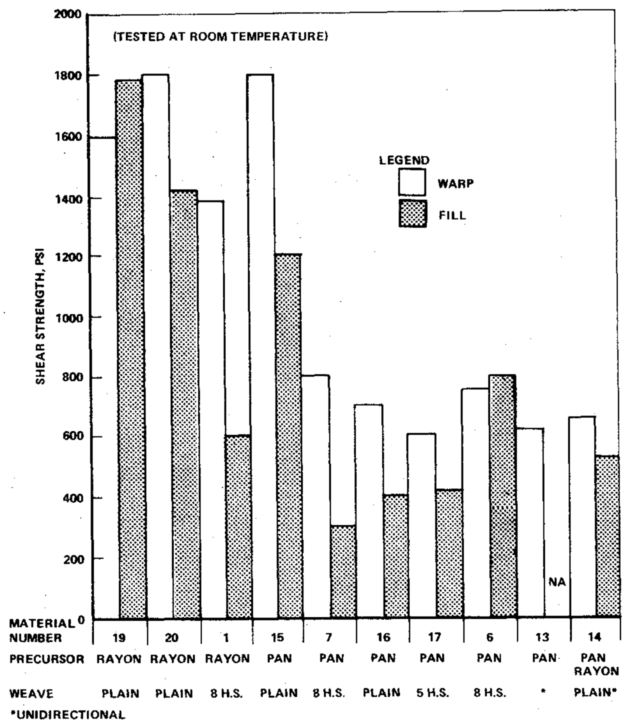


Fig. 2 Interlaminar shear strength for resin/pitch matrices.

When two fabrics are interleaved, it appears that the resulting shear strength is not improved in comparison to the lowest shear strength material. For example, the warp shear strength for material 13 is 656 psi. The (one-to-one) combination of materials 13 and 19 produced a shear strength of 713 psi. The average shear strength of the two would be approximately 1200 psi, based on a shear strength of 1500 psi for material 19. On the other hand, as indicated later, the averaging technique tends to predict better for the cross ply shear strength of interleaved fabrics from more than one material.

Although the shear strengths for the four materials (1, 15, 19, and 20) are significantly better than the other six materials tested, further investigation, holding all but one variable constant, is needed to assign the magnitude of effect on shear strength of precursor weave and fabric thickness. Limited studies using the scanning electron microscope (SEM) have been performed to evaluate failure modes. Figures 3 and 4 are scanning electron microscope (SEM) views of shear interfaces depicting the mode of failure for material No. 1 as filament to matrix. Observation of the failed interfaces of the other

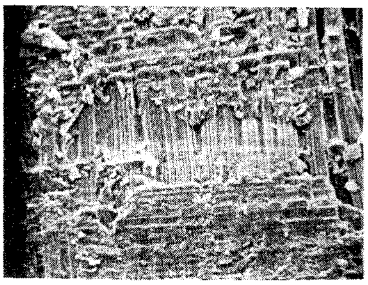


Fig. 3 Scanning electron microscope photograph (265 ×); shear face of interlaminar shear test of material No. 1.

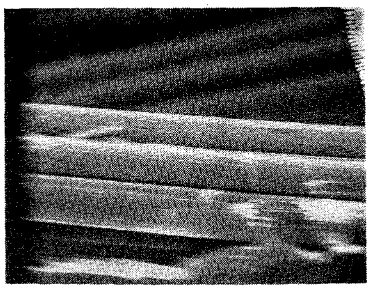


Fig. 4 Scanning electron microscope photograph (2500 ×); shear face of interlaminar shear test of material No. 1.

materials indicates that the primary mode of failure for the resin/pitch matrices is filament to matrix.

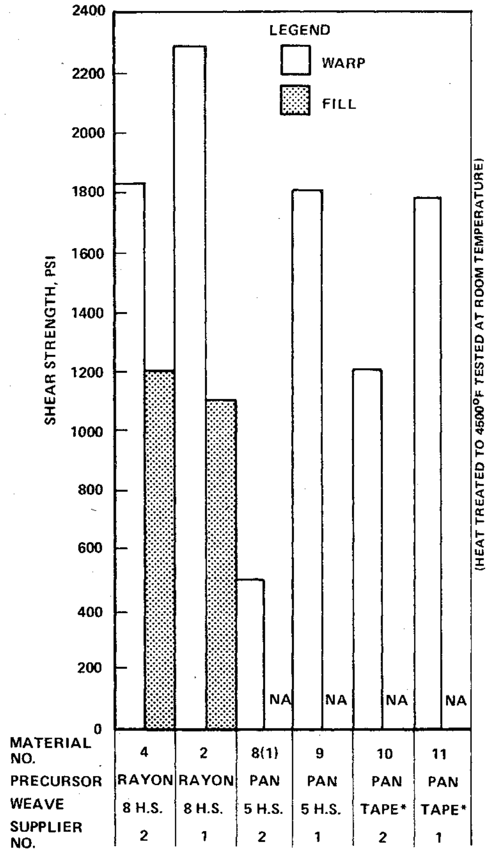
B. Chemical Vapor Deposition: CVD

The processing steps generally followed for the CVD matrix carbon/carbon composites is as follows: 1) layup of dry fabric or tape to the configuration desired, generally on a graphite mandrel, 2) place in furnace and deposite carbon from hydrocarbon gas such as methane, 3) remove from furnace and remove surface buildup of carbon, 4) continue deposition until required density is achieved, and 5) after density is achieved and generally during final deposition, the component is heat-treated to use temperature, generally above 4500°F.

The fiber volume for "dry" CVD processing is generally lower (15-20%) in comparison to resin/pitch matrices. The CVD matrix has characteristics which differ significantly from the resin/pitch matrices. The primary characteristic is the dimensional stability of the matrix and the nature of the matrix buildup. The CVD nucleates at the filament surface and grows outward to fill up the voids between the filaments. There is some dimensional change in the matrix if heated above the deposition temperature; however, the change is significantly less than occurs with thermal decomposition of the resin/pitch matrix. The change in fibers as a result of heat treatment was assumed to be negligible for the comparative analysis.[2]

Figure 5 shows comparative data for shear strength of the CVD matrices, as received from two different material suppliers. As expected, the shear strength of the CVD processed laminates was higher than for the resin/pitch matrices, regardless of the reinforcement. In Fig. 5, one rayon precursor fabric material and one PAN precursor fabric material were compared, as well as one PAN precursor unidirectional tape material.

The heat treatment (exposure to 4500°F) significantly reduced the shear strength of the CVD matrices. This reduction is a result of the dimensional change in the CVD matrix produced by the heat treatment. The structural transformation not only changes the dimensions, but apparently changes the matrix to a more orderly crystalline structure, resulting in a reduction in the shear strength. The non-heat-



(1) FABRIC DESIGNED FOR HIGH CROSS PLY SHEAR STRENGTH FOR USE AS PINS; HOWEVER, THE LOW INTERLAMINAR SHEAR WAS NOT EXPECTED.
* UNIDIRECTIONAL

Fig. 5 Interlaminar shear strength for CVD matrices.

treated shear strength for material No. 3 was 2820 psi (see Table 1). This value is 20% better than the heat-treated version.

The material produced by CVD processing from supplier No. 1 is significantly better than that from supplier No. 2. Since both processes are proprietary, the cause could not be established. (No photomicrographs have been made to observe structure.) The difference is assumed to be related to the deposition process; however, there were some variations and nonuniformity in the density of the composites. Material Nos. 2 and 4 have the same fabric. The shear strength (warp direction) for material from supplier No. 2 was 1860 psi compared to 2346 psi from supplier No. 1 (see Fig. 5). A similar trend existed for the other two materials produced. The shear strength was 533 psi for supplier No. 2 and 1833 for supplier No. 1 for a unidirectional PAN fabric (material Nos. 8 and 9). Similar differences existed for the PAN unidirectional tape (materials 10 and 11).

The deposition temperature and gas flow rates and other conditions are not known; therefore, only the "results" can be compared. The comparative results shown in Fig. 5 show that, for all three reinforcements evaluated, the shear results were higher for material produces by supplier No. 1.

C. Discussion

1) Resin/pitch vs CVD

A comparison of the shear strength values between resin/pitch and CVD matrices with the same reinforcement is shown in Fig. 6. Without exception, the shear strength for the material with the CVD matrix is higher than for the same fabric with the resin/pitch matrix. This is also true for the unidirectional yarn. The shear strength for the yarn resin/pitch is 650 psi, compared to 1950 psi for the same yarn with a CVD matrix.

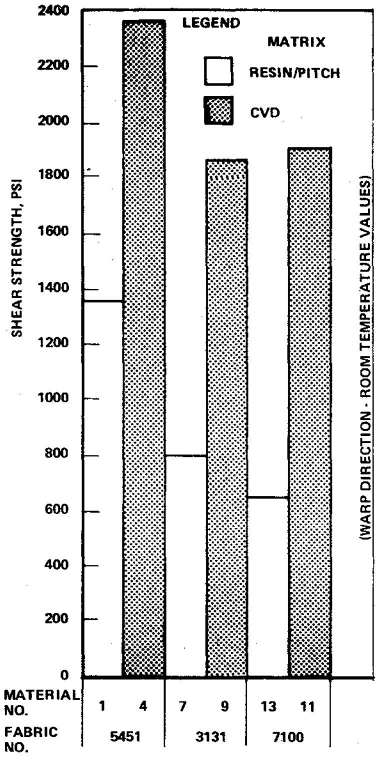


Fig. 6 Comparative interlaminar shear strength for resin/pitch and CVD matrices.

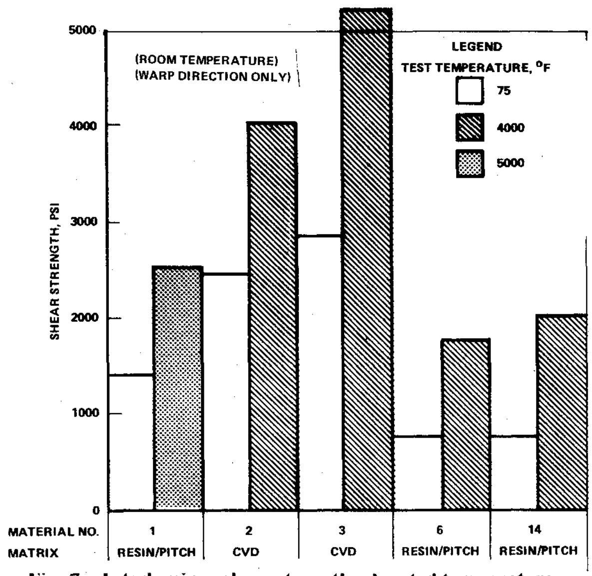


Fig. 7 Interlaminar shear strength, elevated temperature.

2) Resin/pitch vs resin/pitch/CVD

One material, No. 18, was started as a resin/pitch system and final processed by CVD infiltration. The shear strength of the CVD laminate was twice that of the resin/pitch system material (No. 17). The comparative values were 625 psi, compared to 1260 psi. This increase in shear strength indicates that factors other than matrix-to-fiber interface affect the shear strength of carbon/carbon composites. The carbon deposited in the open porosity of the resin/pitch matrix apparently provides some mechanical locking at the layer-to-layer interface. Even more significant may be the interconnection of the CVD, which is deposited continuously in the pores running through the plies, rather than between the plies. The CVD material does not have to be decomposed and therefore stays in the pore and does not shrink away from the pore wall. Possibly, the latter phenomenon offers some potential for improved shear strength, which must be obtained in order to make these materials better suited for rocket nozzle components.

3) Cross ply shear

The cross ply shear is not related specifically to the interlaminar shear; however, it is also a significant factor in the use of carbon/carbon materials. A high cross ply shear strength not only is needed for carbon/carbon pins and bolts, but also is necessary for threads in exit cones and adjacent components. It has been determined that cross ply shear strengths are increased significantly by the use of high modulus fibers. The cross ply shear strengths are listed in Table 1 for 14 of the 20 materials tested. Values range from 2000 to 16,000 psi. The standard graphite fabrics, such as WCA, produces yield cross ply shear strengths of approximately 2500 psi. Conversely, the high modulus unidirectional CVD matrix composites have shear strengths exceeding 16,000 psi. The other materials tested produces cross ply shear strengths between these extremes depending upon 1) concentration of reinforcement, 2) matrix material type, and 3) source or type of reinforcement. In general, CVD produces higher cross ply shear at 10-15% lower fiber concentration than resin/pitch matrices. Non-heat-treated CVD composites were slightly better than similar composites heated to 4500°F. The unidirectional fabric not only is easier to fabricate, but produces higher values than the unidirectional yarn composite.

4) Elevated temperature shear strengths

As for compression, tensile, and flexural strengths, the shear strength of carbon/carbon composites also increases with temperature. Tests were conducted up to and including 5000°F. The results are given in Table 1. Comparisons of room-temperature and elevated-temperature results are shown in Fig. 7. Most of the elevated-temperature tests were conducted at 4000°F; only material No. 1 (rayon precursor with a resin/pitch matrix) was tested at 5000°F. The strength at 5000°F was 75% (1000 psi) better than the room temperature values. The materials tested at 4000°F showed similar increases in shear strength in comparison to the room-temperature shear levels.

The PAN precursor materials (No. 6) showed a 140% increase (735-1780 psi) when the test temperature was increased from room temperature to 4000°F. The combination material (No. 4) increased by 185% (710-2050 psi). In sufficient testing has been completed to establish the increase in strength as a function of temperature. None of the PAN precursors were tested at temperatures above 4000°F.

III. Conclusions

1) The interlaminar shear strength of a carbon/carbon composite is related directly to the concentration of reinforcement in the direction of stress application.

2) Interleaving of fabrics produces a combination which has an interlaminar shear strength near the lowest fabric, rather than an average of the high and low fabrics. The cross ply shear strength tends to be an average of both of the two mixed reinforcements.

3) The CVD produces a higher interlaminar shear composite in comparison to the resin/pitch matrix at approximately the same density, regardless of reinforcement.

4) Heat treating of CVD matrices lowers the shear strength in comparison to the as-deposited strength.

5) In this study, the interlaminar shear strength of carbon/carbon composites increases with temperature up to 5000 °F.

6) The shear strengths of CVD matrices were supplier-related for this study; that is, the values for CVD matrices was consistently higher from one supplier.

References

[1] Davis, H. O., "Selection of Reinforcement for Carbon/Carbon Composites," AIAA Paper 74-1058, San Diego, Calif., Oct. 1974.

[2] Butler, B. L., "Application of Engineering Data on Carbon Fibers to Carbon/Carbon Composites," Sandia Laboratories, Albuquerque, N. Mex., SLA-73-0385B, Sept. 1973.