# ASSESSMENT OF NEW METHOD FOR IMPROVED INTERLAMINAR PROPERTY CARBON-CARBON COMPOSITES

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## Abstract

In a Phase I Small Business Innovative Research (SBIR) contract with the Air Force Research Laboratory (AFRL) at Edwards Air Force Base, a method for improving the interlaminar shear and across-ply tensile strength of two-directional (2-D) fabric reinforced carbon-carbon (C-C) composite materials was devised. The interlaminar reinforced C-C composites were fabricated by SMJ Carbon Technologies using extremely thin, high temperature carbon-carbon veil sheets produced by Energy Science Laboratories, Inc. (ESLI), reinforced in their normal plane with discontinuous carbon fibers and placed between plies of preform layups. Mathematical models for projecting the improved interlaminar strengths were formulated by Materials Research & Design, Inc. (MR&D) and used to predict the A/P tensile and ILS strength improvements. MR&D-predicted and Southern Research Institute (SRI)-measured properties will be presented in this paper. An analytical assessment of the impact of the interlaminar reinforcement on in-plane properties will be also provided, along with a discussion of future potential efforts on this and alternative methods of obtaining improved interlaminar strengths in C-C composites.

## Introduction

The design of carbon-carbon components is a challenging proposition, which is made more difficult by the low interlaminar strength properties of these composites. Carbon-carbon materials are inherently anisotropic, a fact which exacerbates the thermal stresses in both the in-plane and through thickness directions. To accommodate the low interlaminar strength properties, component designs rely on a variety of different methods. A description of conventional material construction approaches, used to circumvent the low interlaminar strength properties of C-C composites, is provided in Table 1 below.

**Table 1.** Conventional methods of C-C material construction used to accommodate low interlaminar strength properties.

| Method | Description | Advantages | Disadvantages |
|---|---|---|---|
| "Shingle angle" layups | Plies are laid up such that they are not parallel to the in-plane direction of the component but rather have in-plane reinforcement that passes at a shallow angle through the thickness of the component | Provides a quantity of through thickness reinforcement for reducing extent of anisotropy of the C-C and for enhanced interlaminar strengths | Manufacturing approach is complex, particularly for axisymmetric bodies of revolution; through thickness reinforcement is provided at the expense of in-plane strength |
| Needled preforms | Needle punching of 2-D woven carbon fabric layers pushes some of the in-plane reinforcement into the through thickness direction. | Through thickness properties are enhanced; preforms are readily available due to extensive use in C-C brake preforms | In-plane properties are sacrificed to achieve the enhanced interlaminar properties |
| Stretch-broken fiber reinforcement | Carbon yarns are stretched to failure and then grouped back together through twisting, much like the formation of natural (e.g., cotton and wool) fibers. Re-joined yarns are then used to construct 2-D fabrics | Fuzziness of the stretch-broken tows after the fibers have been joined back together to form new, round cross-section yarns contributes to the enhanced interlaminar reinforcement. | Since discontinuous yarns are being grouped back together to form the in-plane fiber reinforcement, the in-plane stiffness and the in-plane strength of stretch-broken fabric is compromised. |

In this effort, other approaches for obtaining enhanced interlaminar properties in C-C composites were investigated, including the use of Pyrograf-III carbon nanofiber reinforcement from Applied Sciences, Inc. and a product devised by ESLI and referred to as carbon-carbon veil (CCV) interleaf. With the Pyrograf-III carbon nanofiber reinforcement, concerns were expressed by AFRL relative to the ability of pitch matrix C-C processing methods to maintain orientations of the Pyrograf-III carbon nanofibers normal to carbon fabric plies. Accordingly, the suggestion was made by Dr. Wes Hoffman (AFRL) to make contact with Tim Knowles (ESLI) to investigate whether the flocked fiber product made by ESLI for thermal management applications could be adapted to provide the potential for enhancing C-C composite interlaminar properties. This contact led to the development of the carbon-carbon veil (CCV) interleaf at ESLI. CCV interleaves containing PAN-based (Grafil-34) and CCV interleaves containing pitch (Cytec DKD) fibers were fabricated for use in the C-C composite panel fabrication at SMJ Carbon Technologies.

## Alternative Interlaminar Reinforcement Method: CCV Interleaves

The CCV interleaves consist of carbon paper sheets with flocked discontinuous carbon fibers. This product experiences chemical vapor infiltration (CVI), resulting in thin sheets with discontinuous fibers both in the plane and at some orientation to the veil. When compressed between adjacent carbon fabrics, the CVI bonds break, leaving chopped fibers positioned within adjacent fabric layers. Post compression inspection reveals that the dry fabric plies stick together, and the fabric layers are now fuzzy on both sides. The interleaf has transferred fiber and the carbon fabric surface is coated with the standing discontinuous flocked fibers. Figure 1 below illustrates this successful transfer process onto the 2-D fabric ply surface.

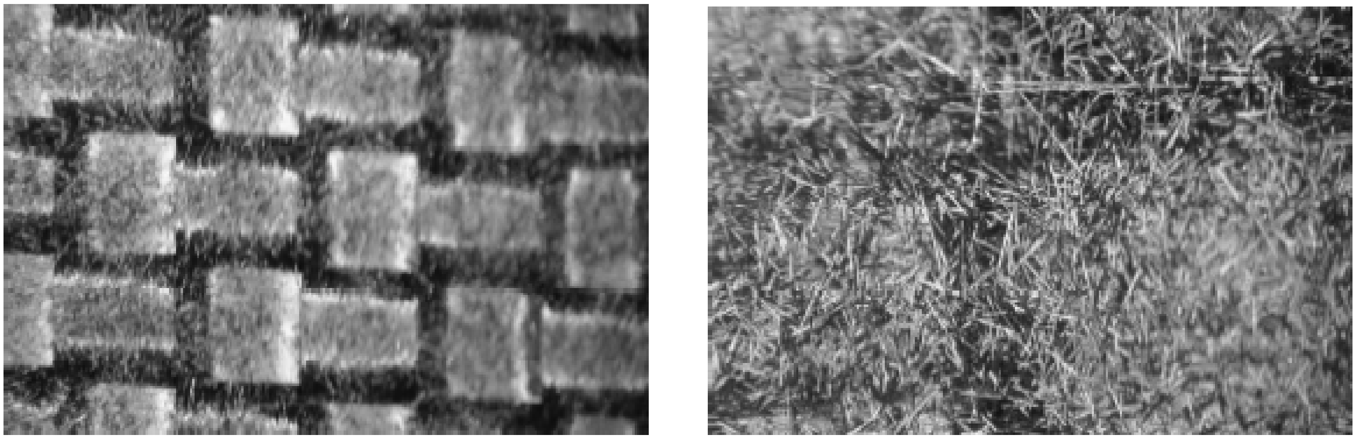
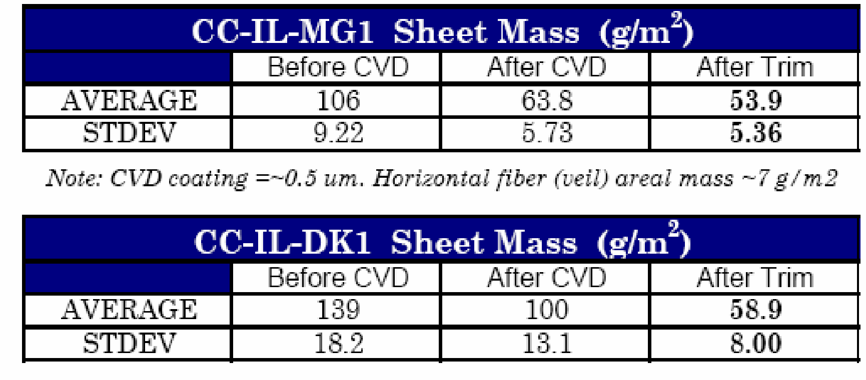


**Figure 1.** Photographs showing successful transfer of discontinuous flocked fibers onto 2-D carbon fabric.

CCV interleaf specimens were fabricated using both pitch and PAN-based discontinuous flocked fibers. Table 2 below provides a description of these two different CCV interleaf constructions.

**Table 2.** Description of CCV interleaf specimens fabricated by ESLI for use in SMJ Carbon Technologies C-C composites.



| CC-IL-MG1 Sheet Mass (g/m$^2$) | Before CVD | After CVD | After Trim |
|---|---|---|---|
| AVERAGE | 106 | 63.8 | **53.9** |
| STDEV | 9.22 | 5.73 | **5.36** |

*Note: CVD coating =~0.5 um. Horizontal fiber (veil) areal mass ~7 g/m2*

Grafil-34 (PAN-based fiber) CCV interleaf specimens

| CC-IL-DK1 Sheet Mass (g/m$^2$) | Before CVD | After CVD | After Trim |
|---|---|---|---|
| AVERAGE | 139 | 100 | **58.9** |
| STDEV | 18.2 | 13.1 | **8.00** |

DKD (pitch fiber) CCV interleaf specimens

MR&D math model calculations were made using information provided by ESLI on the nature of the CCV interleaf constructions. As shown in Figure 2 below, these calculations indicated that significant improvement to the C-C interlaminar tensile strength (ILT) is theoretically possible using the DKD CCV interleaves.

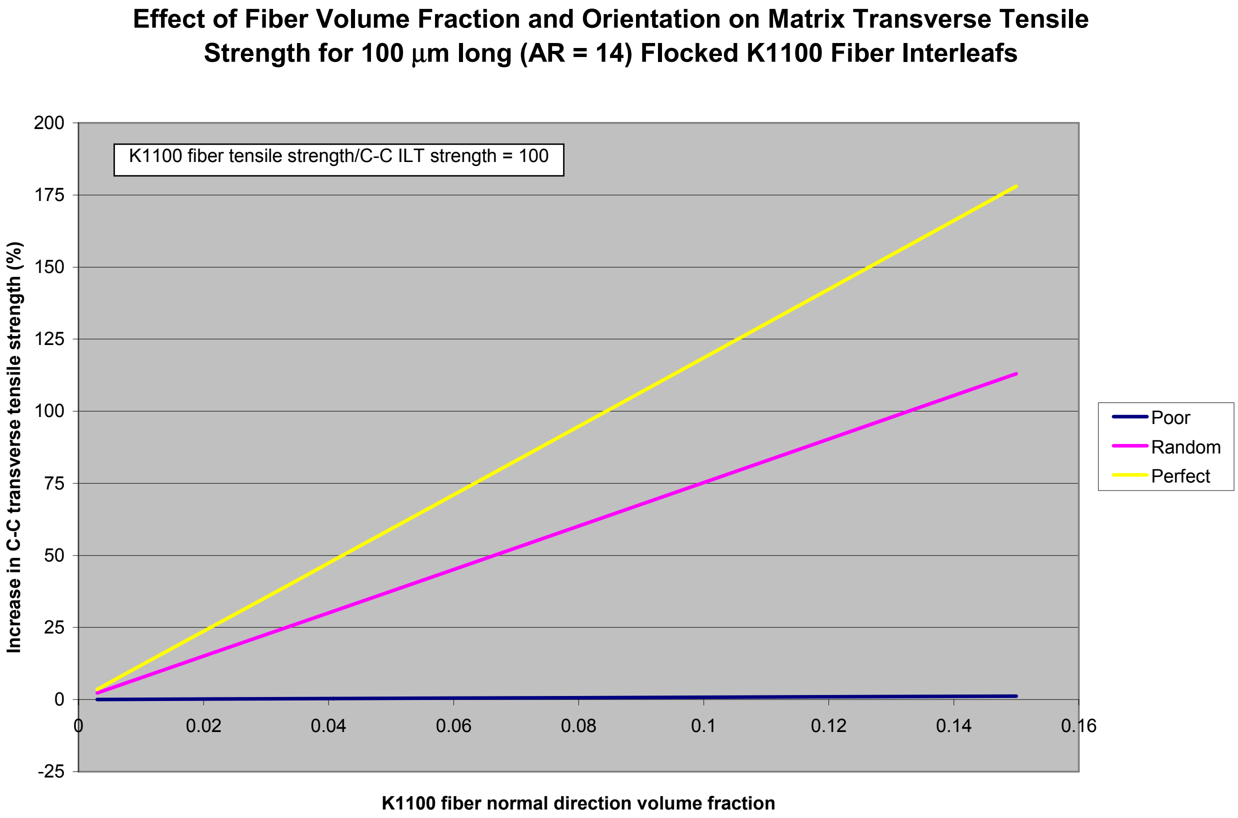


**Figure 2.** Results of MR&D math model calculations indicating potential effect of CCV interleaves on enhanced interlaminar (i.e., through thickness) tensile strength of C-C.

## Carbon-Carbon Fabrication And Testing

Table 3 below summarizes the C-C panels fabricated by SMJ Carbon Technology in the Phase I program. C-C composites were fabricated without the use of CCV interleaves to provide baseline (i.e. no interlaminar reinforcement) properties for the C-C system. Panels containing milled PAN fiber (Grafil-34) and the milled pitch fiber (DKD) were also fabricated. Fabrication of different thickness C-C panels permits through thickness strength tests to provide information on the effect of the fiber volume fraction of the interlaminar reinforcement. For the same volume of CCV interleaves (and fabric plies), the thinner C-C composites will contain a greater volume fraction of through thickness (and in-plane) reinforcement. Both in-plane and through thickness strengths can be calculated from composite property models.

**Table 3.** C-C panels fabricated by SMJ Carbon Technology in Phase I program.

| # of plain weave plies | # of CCV interleaves | CCV interleaf reinforcement | Thickness of C-C panel |
|---|---|---|---|
| 5 | n/a | n/a | 0.080 inch |
| 5 | 4 | DKD | 0.160 inch |
| 5 | 4 | DKD | 0.125 inch |
| 5 | 4 | DKD | 0.100 inch |
| 5 | 4 | DKD | 0.080 inch |
| 5 | 4 | Grafil-34 | 0.160 inch |
| 5 | 4 | Grafil-34 | 0.125 inch |
| 5 | 4 | Grafil-34 | 0.100 inch |
| 5 | 4 | Grafil-34 | 0.080 inch |

The limited testing effort that was conducted by SRI in the Phase I program is summarized in Table 4 below. Both interlaminar tensile and interlaminar shear strength tests were performed. The DKD interleaf material was selected for tests since C-C fabrication of the DKD interleaf materials resulted in higher density and therefore lower porosity levels in the fabricated C-C composites. As evident from Table 3, a considerable quantity of C-C has been fabricated for possible additional testing of material properties of these C-C composites at AFRL.

**Table 4.** Summary of mechanical properties measured on SMJ Carbon C-C composites by Southern Research Institute within Phase I program.

| Test Type | Interlaminar Reinforcement | C-C composite thickness | Replications |
|---|---|---|---|
| Interlaminar tension | None | 0.080 inch | 3 |
| Interlaminar tension | DKD | 0.080 inch | 3 |
| Interlaminar shear | None | 0.080 inch | 3 |
| Interlaminar shear | DKD | 0.080 inch | 3 |

Photomicrographs of the C-C composites fabricated by SMJ Carbon Technologies are provided in Figure 3 and Figure 4. Figure 3 shows the baseline C-C composite without interlaminar reinforcement. Figure 4 shows the C-C composite with the DKD fiber CCV interleaves between the carbon fabric plies. The process used by SMJ Carbon employs naphthalene pitch resin as the matrix infiltrant, which is subsequently pyrolyzed and carbonized. Heat treatment to high graphitization temperatures was employed as necessary, to open up pores to permit matrix infiltration. These panels were made from five plies of T-300 plain weave fabric with ESLI-supplied interleaves between plies, where applicable. The panels were approximately 6” x 6” in the in-plane dimensions.

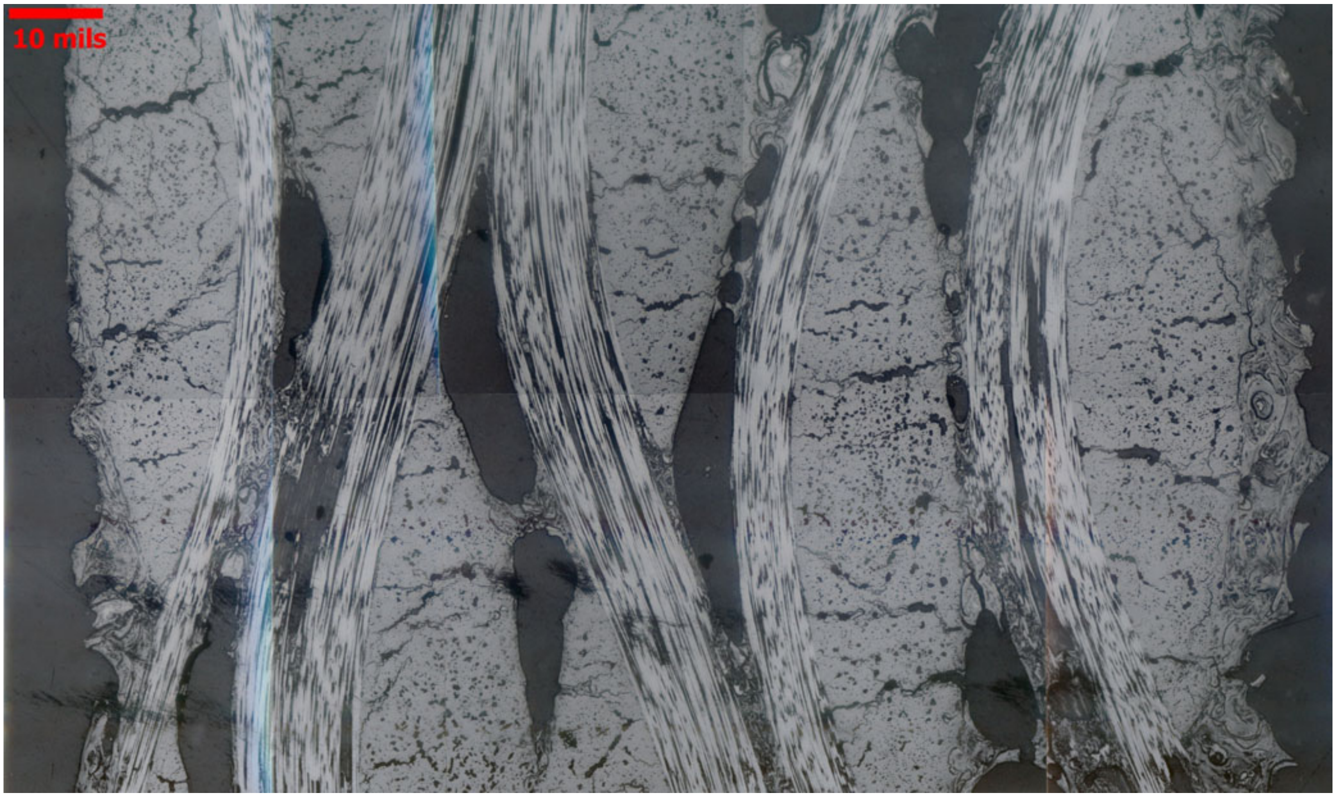


**Figure 3.** Photomicrograph of SMJ Carbon C-C composite without CCV interleaves.

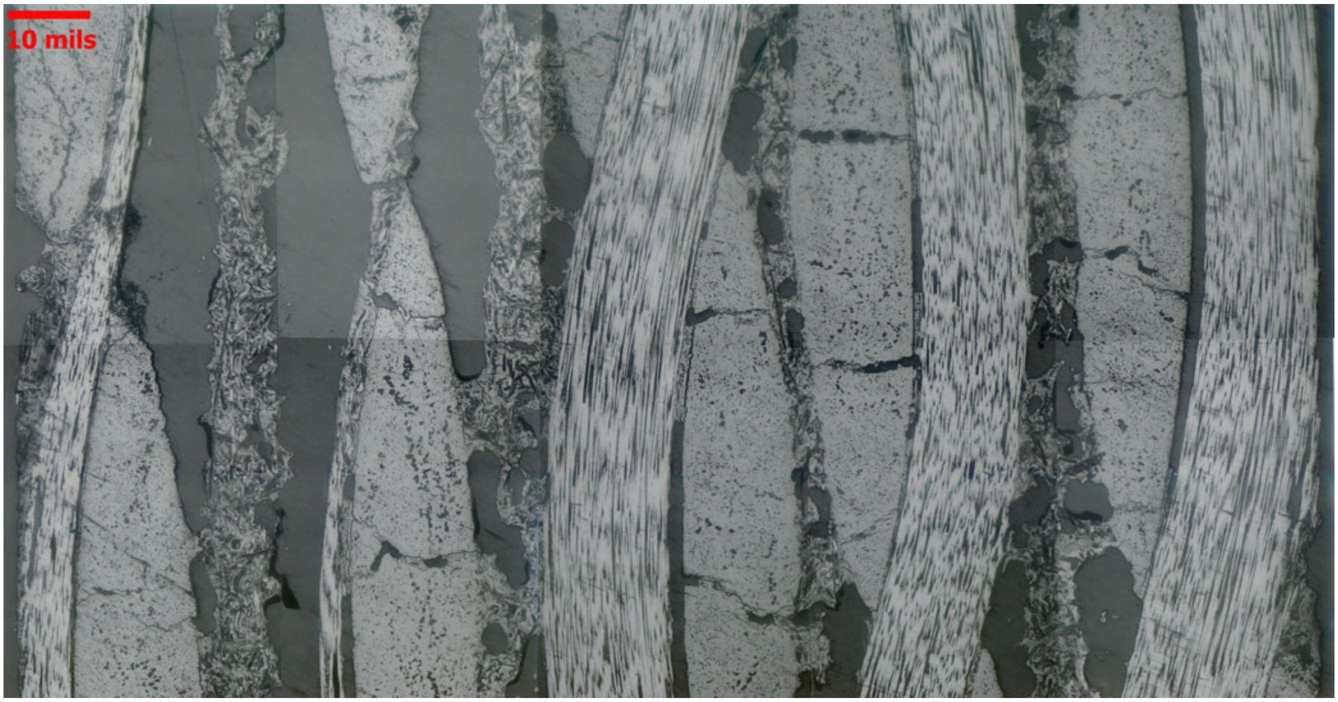


**Figure 4.** Photomicrograph of SMJ Carbon C-C with DKD fiber CCV interleaves.

The measured interlaminar strengths for the baseline C-C were low, due to problems experienced by SMJ Carbon in densifying the panels. A different fabric would have alleviated this problem and would likely have increased all of the interlaminar strengths. As shown in Figure 5 below, the comparisons of CCV interleaf reinforced C-C versus baseline C-C show significant improvement in interlaminar strengths.

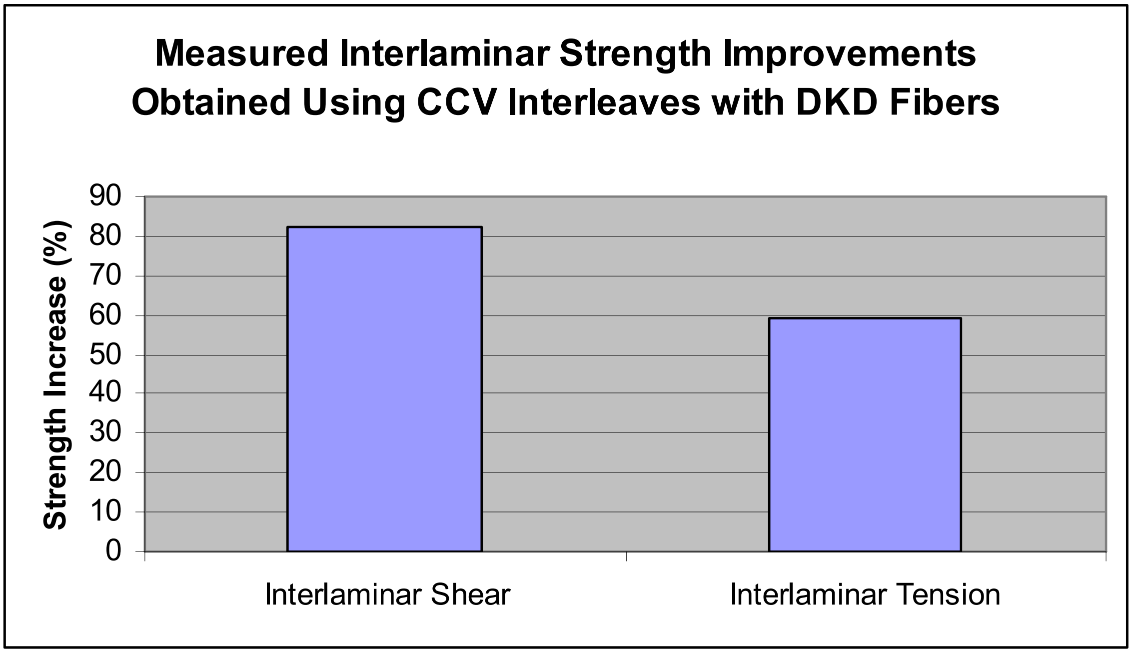


**Figure 5.** Chart illustrating the percent improvement in measured C-C interlaminar shear (ILS) and interlaminar tensile (ILT) strengths achieved with the use of the DKD fiber CCV interleaf reinforcement.

## Post-Test Data Correlation

Correlations were performed using a micromechanics math model to determine effective DKD (pitch) fiber strengths in CCV interleaf materials. The data correlations were performed using known information on the C-C composites, including the fiber volume fractions of T-300 in-plane (0.219) and DKD CCV interleaf reinforcements (0.0832), and the fact that, by ESLI's estimates, approximately 50% of the DKD flocked fibers were oriented in the plane of the T-300 fabric following compaction. Calculations were made varying the estimated values of the unknown parameters. These included a) the percentage of DKD fibers oriented essentially perpendicular (Z direction) to T300 fabric plane, b) the percentage of DKD fibers oriented at a small angle relative to T-300 fabric plane, and c) the average orientation angle of non-Z direction DKD fibers. A sketch of the math model of CCV interleaf and T300 fabric reinforced C-C composite used for the data correlation task is provided in Figure 6 below.

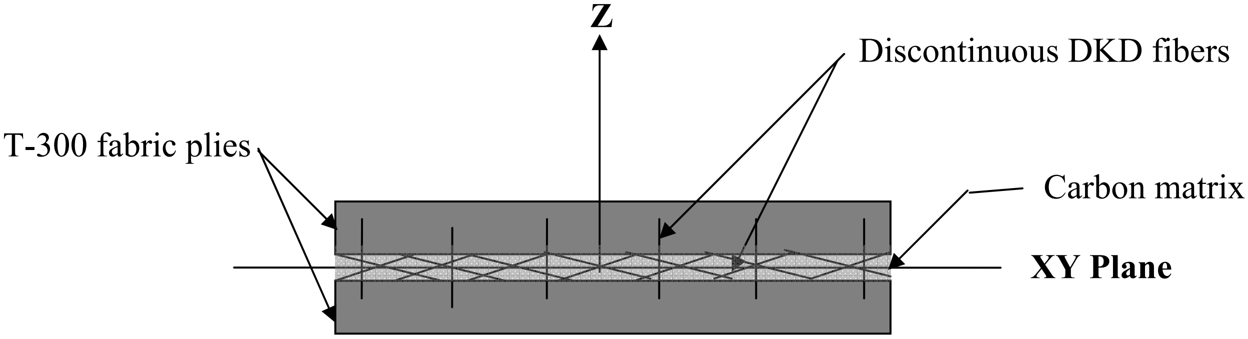


**Figure 6.** Sketch of math model of CCV interleaf and T-300 fabric reinforced C-C composite.

Key assumptions of the model used for the data correlation are the following:

1. The aspect ratio of the DKD filaments is sufficiently high to allow the DKD fibers to experience their full axial load. That is, the shear lag phenomenon occurs over a distance along the DKD fiber that is much shorter than the actual length of the DKD fiber.
2. The model treats the CCV interleaf/T-300 fiber reinforced C-C composite as an assemblage of a large number of fiber/matrix bundles or unit cells oriented in three-dimensional Cartesian space to form a representative volume element (RVE). Thermoelastic properties can be calculated from volume averaging of all the unit cells making up the RVE. Strengths are obtained through stress analysis of the RVE for individual applied loads, e.g. transverse (Z) tension and interlaminar shear. Stresses in each fiber/matrix bundle are transformed to a) bundle axial normal stress, b) bundle transverse normal stress, c) bundle axial shear stress, and d) bundle transverse shear stress. Each of these stresses is then compared to its corresponding strength (e.g., bundle axial tension or compressive strength, bundle transverse tensile strength, bundle axial shear strength, and bundle transverse shear strength, respectively) to determine the value of applied stress leading to failure of the composite. The algorithm for this model's calculations is described in Rosen et al. (1977).

For a given set of the unknown parameters (i.e., the volume fractions of Z and non-Z DKD fibers and the average orientation angle), DKD fiber tensile and compressive strengths were determined in order to match the measured ILT and ILS strengths of the DKD fiber CCV interleaf reinforced C-C materials.

Figure 7 shows the effect of the volume fraction of the Z direction DKD fibers on the calculated effective strengths of the DKD fibers, for an 11.3° average orientation angle of the non-Z DKD oriented fibers. This plot shows that the compressive strength is essentially independent of the percentage of oriented DKD fibers but the DKD tensile strength is very dependent on the percentage of oriented DKD fibers. This is because the C-C ILT strength is governed by the tensile strength of the DKD while the C-C ILS strength depends on the orientation of the DKD fibers and their compressive strength, which is assumed to be lower than their tensile strength.

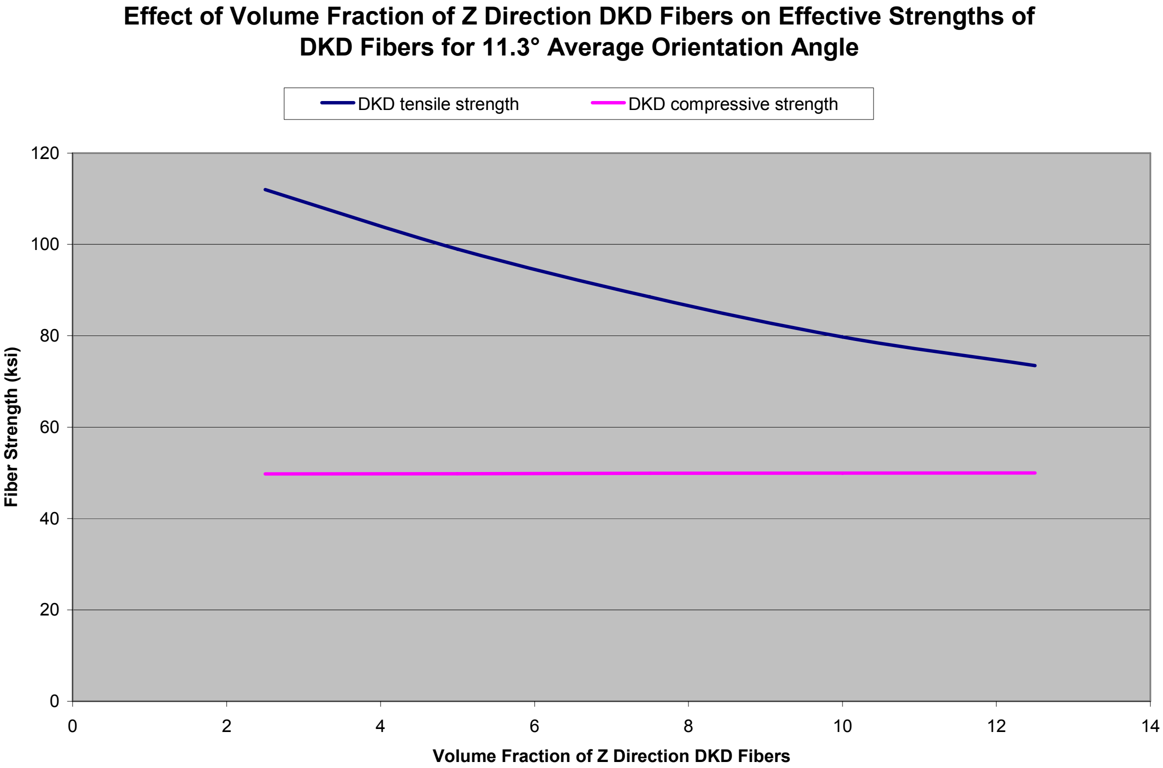


**Figure 7.** Effect of fraction of the Z direction DKD fibers on the calculated effective strengths of the DKD fibers, for an 11.3° average orientation angle of the non-Z DKD oriented fibers.

Figure 8 shows the effect of the average non-Z DKD fiber orientation angle on the effective strengths of DKD fibers for a 2.5% volume percentage of Z direction DKD fibers. This plot shows that the average orientation angle has a relatively insignificant effect on the effective DKD fiber tensile strength, while the effective DKD fiber compressive strength is very sensitive to this orientation angle.

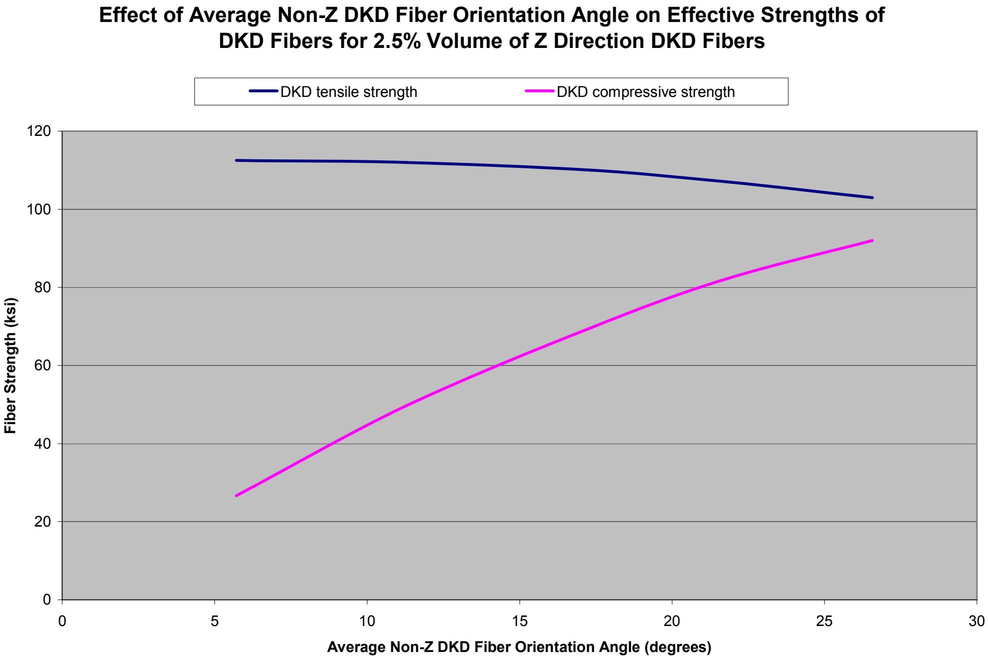


**Figure 8.** Effect of the average non-Z DKD fiber orientation angle on the effective strengths of DKD fibers for a 2.5% volume percentage of Z direction DKD fibers.

A review of available reports on measured mechanical properties of pitch fiber reinforced C-C composites has generated two bounding sets of effective tensile and compressive strengths of pitch fibers. A recent report by Cuneo and Koenig (SRI) on heat treated P-30X pitch fiber reinforced C-C composites resulted in effective high modulus pitch fiber tensile and compressive strengths of 120 ksi and 44 ksi, respectively. A more classic work by Roger Bacon (1989), containing C-C data on heat treated P100 pitch fiber reinforced C-C composites, determined that the effective fiber tensile and compressive strengths of the P100 fibers were 142 ksi and 61 ksi, respectively. In both cases, the effective fiber tensile strength was approximately two and one-half times the effective fiber compressive strength. It is reasonable to conclude that a similar ratio of DKD fiber tensile to DKD fiber compressive strength holds true here.

With these pitch fiber effective tensile (120 to 142 ksi) and compressive (44 to 61 ksi) strengths in mind, and from an examination of Figure 7 and Figure 8, the following conclusions can be made regarding the probable percentage of essentially Z direction DKD fibers and the probable orientation of the non-Z DKD oriented fibers:

1. The volume percentage of the essentially Z direction DKD fibers is approximately 5%.
2. The average orientation angle of the non-Z oriented DKD fibers is in the $10^o$ – $15^o$ range.

Table 5 below summarizes the final set of model parameters.

**Table 5.** Final set of parameters of MR&D math model of CCV interleaf/T-300 fabric reinforced C-C composite.

| Model parameter | Final Value |
|---|---|
| Average orientation angle of non-Z oriented DKD fibers | ~$10^o$ – $15^o$ with respect to the XY fabric plane |
| Percentage of non-Z oriented DKD fibers in CCV interleaves | ~45% |
| Percentage of Z direction DKD fibers in CCV interleaves | ~5% |
| Effective tensile strength of DKD fibers | ~ 110 ksi |
| Effective compressive strength of DKD fibers | ~ 50 ksi |

Finally, an assessment of the effect of the DKD fiber CCV interleaf reinforcement on the in-plane C-C composite properties was performed. From data measured by ESLI on the Phase I effort, the effective thickness of the ~59 g/m$^2$ CCV interleaf under 100 psi of normal direction compression was measured to be 0.0032 inch. For a 30 ends per inch (epi) x 30 epi T-300 1k plain weave fabric typically used in making high performance C-C composites, the areal weight is 157 g/m$^2$ and the thickness is 0.00625 inch, resulting in a 0.557 fiber volume fraction composite. The addition of a 0.0032 inch CCV interleaf means that within a fixed thickness or fixed mass composite, a reduction of 34% in the available continuous T-300 fiber volume fraction would result. This would obviously result in a significant impact to the in-plane tensile and compressive strengths. Accordingly, much lower areal mass and/or much lower effective thickness CCV interleaf materials must be devised for successful implementation of this interlaminar reinforcement method.

## Conclusions

The most important conclusions to be made regarding the technical effort of this Phase I contract are the following:

1) Very thin interlaminar reinforcement sheets containing milled PAN- and pitch-based fibers were successfully fabricated. Compaction of plies containing the thin CCV sheets resulted in a portion of the milled fibers protruding through the fabric, thereby indicating the potential for this product to provide interlaminar reinforcement.
2) Carbon-carbon composites of varying thickness were successfully fabricated using the CCV interleaves between plies of 2-D plain weave fabric reinforcement. A small portion of the fabricated composites were cut up to provide test specimens for interlaminar property measurement. A significant amount of C-C material remains available for property measurements at AFRL.
3) The use of the CCV interleaf reinforcement material has been demonstrated to be an extremely effective method for improving interlaminar strengths of C-C composites. Relative to unreinforced matrix C-C composites, measured improvements were 59% for the interlaminar tensile strength and 82% for the interlaminar shear strength.
4) The MR&D micromechanical models were successful at reproducing the measured interlaminar strengths, through adjustments to the model parameters used to make the pre-test predictions. The model parameters necessary to achieve correlation with the measured data (i.e., effective DKD fiber strengths, percentages of DKD fibers in the ply

normal direction and non-normal directions, and the average orientation angle of the non-Z oriented direction DKD fibers) appear physically reasonable. MR&D therefore has confidence that use of the micromechanical models will allow future predictions of the improvements to C-C composite interlaminar properties through the use of the CCV interleaves. Moreover, design of CCV interleaves using the MR&D micromechanical models appears very achievable.

5) Due to expected reductions in the in-plane properties associated with the Phase I effort CCV interleaf reinforcement, much lower areal mass CCV interleaf materials must be devised for the successful adoption of this technology within the C-C composite community.

## Future Work

A technical plan with the following tasks has been recommended for future efforts in this area:

1. *Math model enhancements and design analyses.* This task will involve improvements to the MR&D mathematical models for predicting interlaminar and in-plane properties, followed by utilization of the models for assisting in the design of the CCV interleaf interlaminar reinforcement.
2. *Continued development and fabrication of reinforcement interleaves.* As discussed above, it is paramount that much thinner and much lower areal mass CCV interleaf materials be devised to minimize the impact of the interlaminar reinforcement on the in-plane composite properties.
3. *Fabrication of C-C composite panels using enhanced interlaminar property preforms.* MR&D has recommended that C-C composites be fabricated using
    a. 2-D carbon fabric and no interlaminar reinforcement,
    b. 2-D carbon fabric and reinforcement interleaf materials of two different types,
    c. 2-D carbon fabric woven using stretch-broken yarns,
    d. Needle-punched 2-D carbon fabric,
    e. Additional preforms of MR&D-proprietary designs.
4. *Mechanical property testing using coupons machined from C-C panels.* MR&D has recommended that mechanical property measurements, including both in-plane and interlaminar properties, be performed to enable an assessment of the improved interlaminar properties and the reductions in in-plane properties associated with all of these composites.
5. *Design of improved interlaminar property C-C component.* Finally, MR&D has recommended that C-C component designs of interest to AFRL be developed for all of these reinforcement methods and their associated composite properties, to obtain an analytical assessment of the minimum weight design achieved by the various reinforcement methods.

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