Relationships in Composite Fabrication and Carbon-Carbon Densification

A Model For Advanced Composite Fabrication And Densification

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All concepts proposed and developed herein are entirely original and are the analysis, perceptions and opinions of Randy Lee

INTRODUCTION

Though it may not be fully realized from a historical perspective, LTV scientists developed the original carbon-carbon composite material back in the 1950's during the Apollo program. Reinforced Carbon-Carbon (RCC) was subsequently developed and introduced for application to the Space Shuttle orbiter's Leading Edge Substructural System (LESS) or outer shell Thermal Protection System. Due to its superior high temperature capabilites, rayon fiber-based RCC was utilized for semi-structrual contoured paneling along the leading wing edges and nose regions of the orbiter to provide primary thermal protection for the ship during re-entry episodes. Low maintenance performance, multiple missions between repair, and fabrication requirements similar to that of fiberglass have given the orbiter's RCC a long history of successful application to the hottest points of the ship. Since the late 1970's, LTV has pursued next generation concepts of this unique material through extensive development efforts aimed at higher strength, primary structural applications utilizing Advanced Carbon-Carbon (ACC). While this PAN fiber-based form of carbon-carbon offers tensile strengths several times greater than RCC, ACC presents a set of challenges quite different than those encountered with the RCC platform. Even though the initial ACC substrate autoclave molding and fabrication process may seem straightforward, its relationship with the subsequent carbon-carbon densification phase and ultimately, the silicon carbide thermal conversion coating process encompasses a number of problems which have yet to be completely solved. It is contended here that tight process controls are required to insure design goals for specific substrate material properties are achievable and reproducible in order to maximize as-molded composite laminate integrity, to minimize the occurrence of in-process or post-process (field) delaminations, and to minimize thermal expansion incompatibilities between the constituents.

In general, reinforced composites often consist of several plies of fabric laminated in a hardened resin matrix where the fibers and fabric provide the substrate with reinforcement properties while the cured polymer resin acts as the composite matrix. In many fiber-reinforced composite systems, porosity is either insignificant or unimportant. Carbon-Carbon composites consist of graphite (carbon) fibers and fabric embedded in a matrix of carbonized resin. The resin precursor is generally from the family of phenol-aldehyde (phenolic) or furfuryl alcohol type polymer systems. Initially, the substrate is simply a graphite fabric / cured organic resin composite but this becomes densified carbon-carbon after several cycles of 1500°F pyrolysis and vacuum/pressure resin impregnation. Each pyrolysis generates porosity throughout the substrate while each impregnation/cure reduces the porosity. In essense, this is the carbon-carbon densification process. The individual pores generally take the form of cavities, tunnels and interconnected voids, and may vary widely in dimension from angstroms to microns. However, it is likely that only pores in the micron range are truely accessible to forced impregnation with fluids as tests have repeatedly shown that various liquids (resins, water, alcohols) are approximately equivalent in terms of volume penetration within the substrate. Indeed, it has been surmized experimentally that liquids do not permeate the entire porosity network within the substrate but are accessible only to the *open porosity*. Obviously, the pores nearest the periphery of the substrate are the most accessible while those farther in are more difficult to permeate. The application of weak vacuum and high pressure during the impregnation process is intended to maximize the effectiveness of the process. Inevitably, a certain volume of the porosity becomes sealed off and permanently present within the composite substrate. This closed porosity is difficult to measure but is suspected to be small when compared to the open porosity. However small, it is a property that must be seriously considered in the formation of useful and reliable carbon-carbon composite structures.

Densification of carbon-carbon substrates is most appropriately defined as *matrix densification* and substrate pyrolysis is nothing more than thermal conversion of the resin matrix into glassy carbon. Pyrolysis of the initial molded article produces a substrate consisting of the original carbon fiber reinforcement and remnants of resin char (glassy carbonized resin) along the walls of a relatively large porous network formed from the thermal release of pyrolysis volatiles. After the first pyrolysis operation, total pore volume is at its highest level throughout the process and the substrate is said to be in the 'first carbon state'. In the next step, vacuum/pressure resin impregation saturates the porosity and the system is said to be in the 'bimatrix state' because the matrix consists of both carbonized resin and fresh resin impregnant. Curing of the impregnant resin produces a small amount of micro-porosity within the resin phase when volatiles and solvents are driven out and the phenolic resin undergoes condensation polymerization/crosslinking producing water. The second pyrolysis step then carbonizes the impregnant resin carrying the substrate to the 'second carbon state'. The amount of porosity generated in the second pyrolysis is notably less than that generated during the first pyrolysis as the density of the substrate increases from one carbon state to the next. It can be shown that successive reductions in porosity over the carbon-carbon densification process tend to follow exponential-type response functions characteristic of processes taking on large values initially and gradually becoming smaller as the theoretical limit is approached.

The bulk density of the substrate is a composite density influenced by the fiber density, the matrix density and the level of pore volume within. The skeletal or true composite density is determined only by the fiber and matrix components. On the average, the thickness of a molded laminate decreases by about 2% from the first pyrolysis and only slightly thereafter (less than 1% across four cycles of densification). Hence, the substrate volume has been found to remain almost constant throughout the densification process, so the final carbon-carbon fiber volume fraction is essentially determined by the initial molding operations or the original design parameters. Fiber weight fraction, matrix weight fraction, matrix volume fraction and the amount of carbon deposited are each expected to change appropriately throughout the densification process. Also, basic mechanical properties of the substrate are expected to improve as densification progresses. It can be shown that substrate densities, weight/volume fractions, carbon gain and even mechanical attributes tend to follow characteristic response curves analogous to the porosity effect descibed above. While the porosity fraction approaches a lower limit over the process, densities and mechanical strengths increase. After four or five cycles of densification, the substrate attains property values not too different than that of the initial molded substrate. However, the process of densification has imparted unique refractory-like properties to the substrate making it quite different than ordinary graphite/resin composites. Ablative capabilities, high temperature stability and integration with ceramic systems gives carbon-carbon the right to truely be classified as an *advanced* composite material.

Over several years of laboratory processing, pilot line development and shop manufacturing of carbon-carbon composite panels and articles, a large data bank has been accumulated reflecting some interesting process trends, particularly those undergoing ACC-type production. Much of the data employed for this report was acquired from a series of ACC Densification Studies designed to examine the behavior of composite physical properties throughout the substrate fabrication and densification process schemes. From the initial molding phase through densification to the final oxidation protective SiC coating process, there has been unanimous agreement that integration of critical process information with relevant material properties is mandatory for the ACC platform to be fully successful. For this study, original concepts were derived by the author and then developed into a systematic *model*, if you will, designed to characterize or simulate the entire process sequence mathematically. Basic principles of general fiber/resin composites are introduced and then further advanced in order to provide representative applications to the specific process of ACC-type carbon-carbon densification. To demonstrate the theory, examples and applications utilize values taken from the ACC data bank which have been reduced to the Table of Averages given in the Procedures & Results section below.

PROCEDURES & RESULTS

Laminates for three separate Densification Studies were processed and tested during the period from 1983 to 1985. In addition, data was accumulated from many other articles processed in both the LESS development lab and the Advanced Carbon-Carbon Technologies (ACT) group throughout the period 1983 to 1987. Articles utilized in the Densification Studies consisted of F-1041 carbon fiber / K640 phenolic resin Fiberite prepreg fabricated in varying thicknesses (generally 6 to 18 plies). Panels were layed up using 7 plies of bleeder/breather canvas and underwent cure cycle 28A (6°F/min temperature rise with 1 hour holds at 180° and 325°, full vacuum and 30psi throughout). Densification consisted of 3 day calcined coke pyrolysis to 1500°F with single phenolic resin impregnation/cures at each carbon state.

Each article was weighed and dimensioned before and after each process step in order to monitor weight gains, weight losses, geometrical bulk density and composite panel thickness. In addition, small coupons were subjected to ASTM C-20 water boil Archimedes-type testing for determination of open porosity at each carbon state. Previously, a number of tests were performed on a Quantachrome Mercury Porosimeter which was found to damage the samples to the point of providing erroneous results thus, the ASTM C-20 technique was deemed the most appropriate test for determination of open (apparent) porosity of resin matrix and carbon-carbon composite samples. Resin content analysis via nitric acid digestion was performed on a limited number of as-molded coupons so only a rough overall average of this critical parameter was available for the study. Mechanical testing at each carbon state included standard ASTM 3 point flexural, short beam shear and interlaminar tensile as performed at room temperature on various Instron and United testing machines.

Data values from all Densification Studies were in good correlation with each other and with most of the historical data in the combined LESS/ACT data bank. For this report, a tedious data reduction and averaging process was first accommplish utlizing all the available data to produce average numerical representations at each process state forming the Table of Averages given below.

Table of Averages for Carbon-Carbon Composite Fabrication and Densification

Physical Property		**Test Method**	**Carbon State *i***					
			A	**0**	**1**	**2**	**3**	**4**
Bulk Density at *i*	%	Weights & Measures	1.59	1.40	1.51	1.60	1.63	1.64
Open Porosity at *i*	%	ASTM Water Boil	4.3	22.3	15.2	8.6	6.2	4.8
Weight Loss from Pyrolysis to *i*	%	Weights & Measures	--------	11.1	5.7	3.5	2.6	1.7
Weight Gain from Impregnation/Cure at *i*	%	Weights & Measures	--------	12.8	6.7	4.5	2.9	--------
Incremental Carbon Weight Gain from (*i*-1) to *i*	%	Weights & Measures	--------	--------	6.6	3.0	2.0	1.2
Cummulative Carbon Weight Gain from 0 to *i*	%	Weights & Measures	--------	--------	6.6	9.8	11.9	13.1
Average Panel Thickness at *i*	mil/ply	Weights & Measures	11.4	11.2	11.2	11.2	11.3	11.3
3 Point Flexural Strength at *i*	KSI	ASTM Mechanical	41.0	7.9	19.5	28.9	35.1	37.8
Interlaminar Tensile Strenghth at *i*	PSI	ASTM Mechanical	509	52	279	488	607	641
Short Beam Shear Strength at *i*	KSI	ASTM Mechanical	1.7	0.2	0.6	1.0	1.1	1.1
Weight Loss from Autoclave Cure to *A*	%	Weights & Measures	21.5	--------	--------	--------	--------	--------
As-Molded Resin Content at *A*	%	ASTM Acid Digestion	26.1	--------	--------	--------	--------	--------
Carbon F-1041 Fiber Density	g/cm^3	Vendor Supplied	1.91	--------	--------	--------	--------	--------
Cured Phenolic Resin Density	g/cm^3	ASTM Water Boil	1.24	--------	--------	--------	--------	--------
Pre-Cured Phenolic Resin Density at 75-78°F	g/cm^3	Weights & Measures	1.08	--------	--------	--------	--------	--------
Phenolic Resin Cure Solids Yield	%	Weights & Measures	72	--------	--------	--------	--------	--------
Charred Phenolic Resin Density	g/cm^3	ASTM Water Boil	1.43	--------	--------	--------	--------	--------
Phenolic Resin Char Solids Yield	%	Weights & Measures	56	--------	--------	--------	--------	--------

DISCUSSION & THEORY DEVELOPMENT

In order to effectively evaluate the behavior between various composite parameters in algebraic terms, it is necessary to assign specific symbols for their representation. This is done immediately below. Afterwards, a few fundamental definitions of fiber/matrix composites are presented and explored followed by an intermediate treatment of proposed principles specific to laminated composite fabrication, carbon-carbon post-processing and ACC manufacturing science. While some of the concepts introduced here are common to all fiber reinforced polymer matrix systems, several original approaches are derived and explored relative to LTV's unique method for producing ACC substrates in preparation for 2900°F pack mix SiC surface conversion processing.

Symbol Designation for Composite Constituents

W = total weight of the composite article or coupon

w_f = weight of fiber in the composite

w_m = weight of matrix in the composite

V = total volume of the composite article or coupon

v_f = volume of fiber in the composite

v_m = volume of matrix in the composite

v_p = volume of porosity in the composite

ρ_b = composite bulk density

ρ_m = matrix density

ρ_f = fiber density

ρ_t = true composite density

Fiber reinforced composites basically consist of two portions by weight (fiber, matrix) and three portions by volume (fiber, matrix porosity).

Percentages of constituents by weight are defined:

fiber weight fraction

$$f_w = \frac{w_f}{W}$$

matrix weight fraction

$$m_w = \frac{w_m}{W}$$

Percentages of constituents by volume are defined:

fiber volume fraction

$$f_v = \frac{v_f}{V}$$

matrix volume fraction

$$m_v = \frac{v_m}{V}$$

porosity fraction

$$p = \frac{v_p}{V}$$

Basic Relationships Between Composite Constituents

The sum of constituents by weight is equal to the total composite weight:

$$w_f + w_m = W$$

The sum of constituents by volume is equal to the total composite volume:

$$v_f + v_m + v_p = V$$

The sum of fractions by weight is unity:

$$f_w + m_w = 1$$

The sum of fractions by volume is unity:

$$f_v + m_v + p = 1$$

Volume fractions can be expressed in terms of their respective weight fractions. Since

$$\rho_f = \frac{w_f}{v_f} = \frac{f_w W}{f_v V} = \frac{f_w}{f_v}\rho_b$$

then

$$f_v = f_w \frac{\rho_b}{\rho_f} = (1 - m_w)\frac{\rho_b}{\rho_f}$$

Likewise,

$$m_v = m_w \frac{\rho_b}{\rho_m}$$

The bulk density is the sum of the products of each constituent density and its respective volume fraction:

$$\rho_b = \frac{w_f + w_m}{V} = \frac{\rho_f v_f + \rho_m v_m}{V}$$

$$\rho_b = f_v \rho_f + m_v \rho_m$$

An analogous expression can be written in terms of weight fractions with inclusion of the porosity fraction:

$$\rho_b = \frac{W}{v_f + v_m + v_p} = \left(f_w \rho_f^{-1} + m_w \rho_m^{-1}\right)^{-1}(1 - p)$$

The density of heat treated carbon/graphite PAN fiber has been reported by the vendor (Fiberite) to be 1.91g/cm^3. In house, fiber density has been difficult to physically measure directly but can be expressed in terms of m_w , ρ_b and ρ_m :

$$\rho_f = (1 - m_w)\left(\rho_b^{-1} - m_w \rho_m^{-1}\right)^{-1}$$

When substrate porosity is relevant, this becomes

$$\rho_f = (1 - m_w)\left[(1 - p)\rho_b^{-1} - m_w \rho_m^{-1}\right]^{-1}$$

Phenolic resin cured at 325°F under 90 psi has been repeatedly determine to have an average density of 1.24g/cm^3. Using the Table of Averages, values of as-molded substrate for density, porosity and matrix weight fraction (resin content) are ρ_b = 1.59g/cm^3, p = 4.3% and m_w = 26.1% respectively from which the fiber density is estimated to be ρ_f = 1.89g/cm^3 and is comparable to the vendor's certified fiber density.

For this discussion, the vendor reported value of ρ_f = 1.91g/cm^3 will be utilized from which the average fiber volume fraction for as-molded substrate becomes

$$f_v = (1 - m_w)\rho_b\rho_f^{-1} = 61.5\%$$

The true composite density refers to the nonporous portion of the substrate and approaches the bulk density when the pore volume approaches zero:

$$\rho_t = \frac{W}{v_f + v_m} = \frac{W}{V - v_p}$$

$$\rho_t = \rho_b(1 - p)^{-1}$$

For ACC-4 substrate (the fifth carbon state) with ρ_b = 1.64g/cm^3 and p = 4.8% (from the Table of Averages), the true composite density is estimated to be ρ_t = 1.72g/cm^3.

Subscript Designation for Composite Fabrication and Carbon-Carbon Processing

Physical properties and process values can be accompanied by a subscript representing any particular process state to which they apply as the table below illustrates:

State	**As-Molded**	**ACC-0**	**ACC-0 BIM**	**ACC-1**	**ACC-1 BIM**	**ACC-2**	**ACC-2 BIM**	**ACC-3**	**ACC-3 BIM**	**ACC-4**
Description	**As-Molded**	**1st Carbon State**	**1st Impregnation**	**2nd Carbon State**	**2nd Impregnation**	**3rd Carbon State**	**3rd Impregnation**	**4th Carbon State**	**4th Impregnation**	**5th Carbon State**
Subscript	A	**0**	$0B$	**1**	$1B$	**2**	$2B$	**3**	$3B$	**4**

BIM (bimatrix) refers to the cured state, after the resin has been hardened by adequate thermal curing, while states prior to cure will be designated with the prime superscript ′ which represents states consisting of neat, liquid resin prior to cure. Subscripts (and superscripts) may be used to specify any state throughout the entire process sequence and for any value that changes from state to state such as simple substrate weight:

$$\begin{tikzcd}
\underset{\text{Prepreg Lay-Up}}{W_A'} \arrow[r] & \underset{\text{Cured Substrate}}{W_A} \arrow[r] & \underset{\text{ACC-0}}{W_0} \arrow[r] & \underset{\text{ACC-0 BIM}'}{W_{0B}'} \arrow[r] & \underset{\text{ACC-0 BIM}}{W_{0B}} \arrow[r] & \underset{\text{ACC-1}}{W_1} \arrow[r] & \underset{\text{ACC-1 BIM}'}{W_{1B}'} \arrow[r] & \underset{\text{ACC-1 BIM}}{W_{1B}} \arrow[d, bend left] \\
{} & \underset{\text{ACC-4}}{W_4} \arrow[l] & \underset{\text{ACC-3 BIM}}{W_{3B}} \arrow[l] & \underset{\text{ACC-3 BIM}'}{W_{3B}'} \arrow[l] & \underset{\text{ACC-3}}{W_3} \arrow[l] & \underset{\text{ACC-2 BIM}}{W_{2B}} \arrow[l] & \underset{\text{ACC-2 BIM}'}{W_{2B}'} \arrow[l] & \underset{\text{ACC-2}}{W_2} \arrow[l]
\end{tikzcd}$$

Vendor Certified Prepreg Materials and Constituents for Composite Fabrication

Certified Volatile Content is defined by the vendor (Fiberite) as the weight loss upon curing a single ply to 325°F (no vacuum or pressure applied). The test is performed by weighing the ply before and after cure.

Certified Resin Content is defined by the vendor (Fiberite) as the weighed resin content after a single ply is cured to 325°F (no vacuum or pressure applied). The test utilizes results from the Certified Volatile Content and an indirect approach for determining the weight of resin in the sample. This method is descibed below.

Autoclave Fabrication of Woven Carbon Fabric / Phenolic Resin Laminated Substrates

Fabrication of the substrate involves the vacuum bag / pressure molding of several plies of resin-impregnated graphite fabric to the cured state under time controlled conditions of applied temperature and pressure inside a specialized composite curing chamber called an autoclave. Articles may also be manufactured in a heated hydraulic press system but this study deals only with autoclave fabricated substrates. Standard autoclave cure conditions for ACC material consist of full vacuum and 30 psi applied pressure to a bagged laminate of several prepreg fabric plies while raising the temperature to 325°F on a specific time/temperature profile (5° to 10°F / minute with 1 hour holds at 180° and 325° is typical). Common prepreg lay-up patterns include 90°/90° (90°crossply), 45°/45° (45° crossply) and 0°/0° (0° parallel). Typical lay-up configurations for most panels of simple geometry consist of positioning one face of the prepreg on top of a releaseable aluminum tool and then applying a ply of teflon release fabric to the prepreg followed by several plies of bleeder/breather material (such as canvas) prior to vacuum bagging and sealing of the lay-up with plastic film and temporary adhesive tape. The article undergoes a significant weight loss due to the curing process with the release of resin volatiles and the loss of resin into the bleeder material (discussed below). The prepreg lay-up may be conditioned prior to cure by utilizing one or more steps of room temperature vacuum bag de-bulking which compress or compact the plies closer together. Time/temperature profiled heat staging of free prepreg material prior to lay-up may also be employed to partially advance polymerization of the resin (increasing its viscosity) thus enhancing resin distribution and resin flow during the curing process which ultimately affect the distribution of resin content throughout the fully cured article.

The fraction of weight loss a laminate experiences during autoclave cure (to the as-molded state) is the difference in laminate weight before and after cure divided by the weight before cure (the prepreg lay-up weight). If we let η represent the absolute value of fractional weight change a given substrate undergoes and use the subscript l to denote weight loss, then composite weight loss upon autoclave cure can be written as:

$$\eta_{lA} = \frac{W_A' - W_A}{W_A'}$$

When multiplied by 100, η_{lA} simply defines the *positive* value for % weight loss that the substrate undergoes when processed via autoclave cure to the as-molded or A state.

From the Table of Averages, the average weight loss on cure is η_{lA} = 21.5%. In comparison to subsequent weight losses which will be defined shortly, η_{lA} is more complex since vacuum bagged laminates release more than simple resin volatiles during the autoclave cure. Free standing phenolic resin cured under pressure will expel water (reaction product), solvents and volatile monomers. In addition to these molecules, laminates layed-up with bleeder materials cured under full vacuum and pressure throughout will release some of the larger and less volatile components (dimers, trimers, additives), all of which tend to separate out as the various entities move through fabric at different speeds (similar to the separation effect in a chromatography column). Cure cycle studies have demonstrated this effect when bagged lay-ups were removed at various points in the cure cycle and examined prior to complete cure. Not only will resin content vary from region to region within a panel, but resin composition will vary also.

Resin content of the substrate after autoclave cure is defined as the as-molded matrix weight fraction:

$$m_{wA} = 1 - f_{wA} = 1 - \frac{w_f}{W_A}$$

The ASTM nitric acid digestion method has been employed more recently to determine m_{wA}, and with apparently good success. The test requires a dry specimen weight W_A obtained prior to acid digestion and the corresponding fiber weight w_f after complete digestion of the resin in the sample. The average resin content of a few recent samples is $m_{wA} = 26.1\%$ when cured under standard ACC autoclave cure conditions (as given in the Table of Averages). However, this important property varies within a given substrate depending on the specific autoclave fabrication parameters, article configuration, shape complexity and laminate thickness from region to region. Resin starved and resin rich regions are present in almost every composite fabricated throughout industry. Notable commonalities include high resin content in thick regions, near the center of panels and inner radius areas, with low resin content in thin regions, near peripheries and outer radius areas. Ultimately, localized values for m_{wA} may prove to be one of the most unique properties affecting the behavior of composite substrates as they progress through the carbon-carbon densification phase.

The vendor's Certified Resin Content is not very coherent with ACC processing methods and is considered to be less practical since it requires two separate tests for w_f and W_A :

$$m_{wA}^{15psi} = 1 - \frac{w_f}{W_A} = 1 - \frac{w_f}{W_A'\left(1 - \eta_{lA}^{15psi}\right)} = \frac{W_A'\left(1 - \eta_{lA}^{15psi}\right) - w_f}{W_A'\left(1 - \eta_{lA}^{15psi}\right)}$$

where W_A' is the weight of a single ply prepreg sample before treatment with a solvent to remove the uncured resin from which w_f is obtained and then in a separate test, sample weight loss η_{lA}^{15psi} is determined for a single ply prepreg sample cured to 325° at ambient pressure (about 15psi).

The actual resin content of a laminated substrate article at state A can be expressed in terms of vendor certified test values by using the as-molded substrate weight loss η_{lA} typically obtained during autoclave cure of the article by measuring the before and after weights:

$$m_{wA}^{15psi} = 1 - \frac{w_f}{W_A'\left(1 - \eta_{lA}^{15psi}\right)} = 1 - \frac{w_f\left(1 - \eta_{lA}\right)}{W_A\left(1 - \eta_{lA}^{15psi}\right)} = 1 - \left(1 - m_{wA}\right)\frac{\left(1 - \eta_{lA}\right)}{\left(1 - \eta_{lA}^{15psi}\right)}$$

from which

$$m_{wA} = 1 - \frac{\left(1 - m_{wA}^{15psi}\right)\left(1 - \eta_{lA}^{15psi}\right)}{1 - \eta_{lA}}$$

Using this formula, an article fabricated from prepreg of 37% Certified Resin Content and 7% Certified Volatile Content which undergoes 21.5% weight loss on autoclave cure is estimated to have an average ACC as-molded resin content of 25.4%.

Densification of As-Molded Composite Substrates into Advanced Carbon-Carbon

A single densification cycle consists of the following sequence. Pyrolytic conversion (pyrolysis) of the cured composite article to 1500°F over a specific time/temperature profile either in a retort containing the article within a packed media of calcined coke particles (3 day typical) or with continuously flowing inert gas (10 hour developmental). The process results in a significant weight loss and produces a composite substrate consisting of carbon fiber, carbonized resin and porosity (hence the term carbon-carbon). Pyrolysis is followed by forced resin impregnation into the substrate inside a pressure chamber via applied vacuum (about 28 inHg), resin intrusion, venting and then 90 psi applied pressure for 30-60 minutes. After venting and opening the chamber, excess resin is physically removed from the panel surfaces. Finally, the article is placed inside a cureclave and cured to 325°F under 90 psi pressure over a specific time/temperature profile (similar to the autoclave profile discussed earlier). Weights and measures are typically obtained before and after each step. Repetition of the pyrolysis/impregantion/cure cycle produces *densified* carbon-carbon with high mechanical and thermal properties. Design requirements specify the particular number of cycles, not only for mechanical considerations, but to optimize other critical properties (density, porosity, matrix content) which highly impact the susceptibility for successful ceramic coating of the substrate. Historically, under or over densified material has produced undesirable results when subjected to typical Type IV pack mix coating operations. Standard densification runs are 3 cycles for RCC material (designated RCC-3) and 4 cycles for ACC (designated ACC-4). ACC-5 and ACC-6 trials have been investigated in the past and techniques are being explored to reduce the total number of required cycles.

Pyrolysis of As-Molded Articles to the ACC-0 State (First Carbon State)

The fraction of weight loss an as-molded substrate experiences during pyrolysis to the state 0 is the positive difference in substrate weight before and after pyrolysis divided by the former (as-molded) weight:

$$\eta_{l0} = \frac{W_A - W_0}{W_A}$$

The original as-molded substrate weight changes by $W_A = W_0(1 - \eta_{l0})^{-1}$. η_{l0} is a measure of the change in matrix weight fraction from state A to state 0:

$$\eta_{l0} = \frac{(w_f + w_{mA}) - (w_f + w_{m0})}{W_A} = \frac{(w_{mA} - w_{m0})}{W_A} = \Delta m_{wA \to 0}$$

η_{l0} can also be defined by realizing that the matrix of the composite at the first carbon state consists of charred resin remnants from the as-molded state. The weight of carbon at the ACC-0 state is then

$$w_{c0} = y w_{mA}$$

where $w_{c0} = w_{m0}$ can be used interchangably and y is the fraction of carbonized resin remaining after pyrolysis of a small sample to 1500° under standard pyrolysis conditions (ie... the resin char yield, $y = w_c / w_r$). Resin char yield measurements for the particular phenolic resin used in carbon/carbon processing have repeatedly shown that y $\cong$ 56% over the average lifetme of the resin. Using this approach, substrate weight loss from state $0B$ to state 1 can be expressed as a function of the as-molded matrix weight fraction:

$$\eta_{l0} = \frac{(w_{mA} - w_{m0})}{W_A} = m_{wA} - \frac{y w_{mA}}{W_A}$$

$$\eta_{l0} = m_{wA}(1 - y)$$

Using the average resin content of m_{wA} = 26.1% discussed earlier, the expected weight loss from pyrolysis to the first carbon state is η_{l0} = 11.5% which agrees well with the table value of 11.1%

The matrix weight fraction at state 0 (ACC-0 carbon content) can be estimated in terms of the original resin content (as-molded matrix weight fraction):

$$m_{w0} = 1 - \frac{w_f}{W_0} = 1 - \frac{w_f}{W_A(1 - \eta_{l0})} = 1 - \frac{f_{wA}}{1 - \eta_{l0}}$$

$$m_{w0} = 1 - (1 - m_{mA})(1 - \eta_{l0})^{-1}$$

$$m_{w0} = 1 - (1 - m_{mA})[1 - m_{wA}(1 - y)]^{-1}$$

With m_{wA} = 26.1% , the estimated matrix (carbon) content at state ACC-0 is m_{w0} = 16.5%.

m_{w0} (or m_{c0}) is the fraction of charred resin (glassy carbon) remaining (deposited) after pyrolysis of the as-molded article to the ACC-0 state. While nitric acid will readily attack and dissolve cured polymer resins when heated, carbon forms are completely inert to hot acids, ie...acids will digest almost all organic polymers but have no effect on graphites, glassy carbons or amorphous carbons. Thus, matrix content of substrates at pure carbon states must be determined by other methods and the formula above provides an easy approach for estimating carbon matrix content after accurate measurements for as-molded resin content have been obtained.

ACC-0 carbon substrates consist of the lowest matrix (carbon) content, the lowest density and the highest porosity throughout the entire manufacturing process. Structurally, they are not very useful. Densification is required to impart relevant mechanical properties to the substrate.

At ACC-0 (carbon state 0), the true density of the composite consists heavily of fiber and porosity and can be estimated by using values from the Table of Averages for ρ_{b0} = 1.40g/cm^3 and p_0 = 22.3%:

$$\rho_t = \rho_{b0}(1 - p)^{-1} = 1.80\text{g/cm}^3$$

Also, the fiber volume fraction estimated for average ACC-0 substrates with m_{w0} = 16.5% is:

$$f_{v0} = (1 - m_{w0})\rho_{b0}\rho_f^{-1} = 61.2\%$$

As mentioned earlier and treated later in the report, the fiber volume fraction is expected to remain essentially constant throughout the densification process due to negligible substrate volume changes.

Resin Impregnation of ACC-0 Substrates to the ACC-0 BIM State

The fraction of weight gain an ACC-0 substrate experiences from impregnation/cure to the ACC-0 BIM state is the positive difference in substrate weight before and after impregnation/cure divided by the former (ACC-0) weight. If we use the subscript g to denote weight gain, then composite weight gain upon resin impregnation and cure can be written as:

$$\eta_{g0} = \frac{W_{0B} - W_0}{W_0}$$

When multiplied by 100, η_{g0} simply defines the *positive* value for % weight gain at the 0 state. The ACC-0 carbon substrate weight changes by $W_0 = W_{0B}(1 + \eta_{g0})^{-1}$ and the original as-molded substrate changes by $W_A = W_{0B}(1 - \eta_{0l})^{-1}(1 + \eta_{go})^{-1}$.

η_{g0} is a measure of the change in matrix weight fraction from state 0 to state $0B$:

$$\eta_{g0} = \frac{(w_f + w_{r0B} + w_{c0}) - (w_f + w_{c0})}{W_0} = \frac{w_{r0B}}{W_0} = \Delta m_{w0 \to 0B}$$

where w_{r0B} represents the weight of impregnating resin and w_{c0} the weight of previously formed glassy carbon in the ACC-0 article (the matrix weight fraction, w_{m0}). Recall that in the bimatrix state, the matrix consists of both resin and carbon. Symbolically, the ACC-0 BIM matrix weight fraction can be represented as $m_{w0B} = c_{w0} + r_{w0B}$.

Estimations of expected weight gains due to the impregnation process might be feasible when other properties of the substrate are already known (namely porosity and bulk density). Consider the hypothetical case where the measured open pore volume is assumed to be equivalent to the uncured resin volume that has been forced into the substrate under vacuum and pressure:

$$v_{p0} = v'_{r0B}$$

$$p_0 V_0 = \frac{w'_{r0B}}{\rho'_r}$$

where ρ'_r is the uncured resin density which has been repeatedly determined to be ~ 1.08g/cm^3 at 75°-78°F.

$$\frac{p_0 W_0}{\rho_{b0}} = \frac{w_{r0B}}{s\rho'_r}$$

where s is the fraction of cured resin remaining after curing a small sample of resin to 325°F under 90psi (ie... the resin cure yield or resin solids, $s = w_r / w'_r$). Resin solids measurements for the particular phenolic resin used in carbon/carbon processing have repeatedly been found to be ~ 72% over the average lifetime of the resin. Continuing on with the equivalency,

$$p_0 W_0 \rho_{b0}^{-1} = w_{r0B}\left(s\rho'_r\right)^{-1}$$

$$\frac{w_{r0B}}{W_0} = s p_0 \rho'_r \rho_{b0}^{-1}$$

from which

$$\eta_{g0} = s p_0 \rho'_r \rho_{b0}^{-1}$$

If ACC-0 bulk density and porosity have been previously determined, this formula could permit one to make a rough prediction for the expected weight gain from impregnation/cure. From the Table of Averages for ACC-0 substrate, p_0 = 22.3% and ρ_{b0} = 1.40g/cm^3 from which the expected weight gain after the first impregnation/cure is η_{g0} = 12.4% which compares well with the table value of 12.8%.

At the 0B state, the matrix of the composite is the sum of impregnated resin and previously deposited carbon, $w_{m0B} = w_{r0B} + w_{c0}$ by weight and $v_{m0M} = v_{r0B} + v_{c0}$ by volume. Curiously, the bimatrix density has sometimes been suggested as an important value to know. However meaningful this parameter may or may not be, the bimatrix density at state 0B can be approximated by recalling that

$$m_{w0} = \frac{w_{c0}}{W_0} \qquad \text{and} \qquad \eta_{g0} = \frac{w_{r0B}}{W_0}$$

And since

$$\rho_{r0B} = \frac{w_{m0B}}{v_{r0B} + v_{c0}} = \frac{w_{m0B}}{w_{r0B}\rho_r^{-1} + w_{c0}\rho_c^{-1}} = \frac{w_{r0B}}{w_{m0B}}\rho_r + \frac{w_{c0}}{w_{m0B}}\rho_c$$

Then

$$\rho_{m0B} = \left[\left(1 + m_{w0}\eta_{g0}^{-1}\right)^{-1}\rho_r^{-1} + \left(1 + \eta_{g0} m_{w0}^{-1}\right)^{-1}\rho_c^{-1}\right]^{-1}$$

Phenolic resin pyrolyzed to 1500° under standard process conditions has been determined, on several occassions, to have a density of $\rho_c \cong 1.43$g/cm^3. For an ACC-0 BIM substrate of carbon content $m_{w0} = 16.5\%$ and cured impregnant resin weight gain of $\eta_{g0} = 12.8\%$, the overall density of the two-phase matrix density after the first impregnation/cure is $\rho_{m0B} = 1.34$g/cm^3.

Double impregnation/cure procedures performed back to back on substrates in the ACC-0 state have been practiced by both the LESS and ACT groups until recently. When multiple impregnation/cures are performed prior to pyrolysis, state designation can be represented as $0B1$, $0B2$, $0B3$, etc... and incremental weight gains by η_{g01} , η_{g02} , η_{g03} , etc...

If the total composite volume remains approximately constant throughout the impregnation/cure process, the original pore volume is equal to the cured resin volume after the first impregnation/cure plus the additional uncured resin volume from the second impregnation, that is

$$v_{p0} = v_{r0B1} + v'_{r0B2}$$

$$p_0 W \rho_{b0}^{-1} = w_{r0B1} + \frac{w'_{r0B2}}{\rho'_r}$$

$$p_0 \rho_{b0}^{-1} = \eta_{g01}\rho_r^{-1} + w_{r0B2} W_0^{-1} \rho_r^{-1} s^{-1}$$

and since

$$\eta_{g02} = \left(W_{0B2} - W_{0B1}\right) W_{0B1}^{-1} = w_{r0B2}\left[W_0\left(1 + \eta_{g01}\right)\right]$$

then

$$\eta_{go2} = s\rho'_r\left(p_0\rho_{b0}^{-1} - \eta_{g01}\rho_r^{-1}\right)\left(1 + \eta_{g01}\right)^{-1}$$

Using $p_0 = 22.3\%$, $\rho_{b0} = 1.40$g/cm^3 and $\eta_{g01} = 12.8\%$ from the Table, substrate weight gain from the second impregnation/cure is estimated to be $\eta_{g02} = 3.9\%$. Historically, recorded weight gains for a second impregnation/cure at the ACC-0 BIM state have been in the 2-4% range. However, there is indication that some of the inner most pore volume may not be totally accessible to the second impregnation and thus becomes tightly sealed or shielded after the first impregnation/cure. If this is the case, even a very small level of sealed pore volume can have catastrophic effects downline. Trapped volatiles which have not been allowed to adequately expel via pyrolysis after the first impregnation/cure may induce internal stresses resulting in weak planes or possibly delaminations when finally forced out in a subsequent pyrolysis. Meaningful benefits from back-to-back impregnation/cure approaches, if any, are not fully understood and are not recommended for application at any carbon state. For this discussion, only single impregnation/cure cycles will be considered at each carbon state and the subscript nomenclature introduced above can be ignored.

The matrix weight fraction at the $0B$ state after a single impregnation/cure with $\eta_{g0} = 12.8\%$ and $m_{w0} = 16.5\%$ consists of previously carbonized resin from the as-molded state deposited carbon (c_{w0}) and freshly cured resin from the recent impregnantion/cure process and can be estimated by realizing that:

$$m_{w0B} = 1 - \frac{w_f}{W_{0B}} = 1 - \frac{w_f}{W_0\left(1 + \eta_{g0}\right)} = 1 - f_{w0}\left(1 + \eta_{g0}\right)^{-1}$$

$$m_{w0B} = \frac{\eta_{g0} + m_{w0}}{1 + \eta_{g0}} = 26.0\%$$

Pyrolysis of ACC-0 BIM Impregnated Substrates to the ACC-1 State (Second Carbon State)

The fraction of weight loss an ACC-0 BIM substrate experiences from pyrolysis to the ACC-1 carbon state is a measure of the change in matrix weight fraction from state 0B to state 1:

$$\eta_{l1} = \frac{W_{0B} - W_1}{W_{0B}} = \frac{\left(w_f + w_{c0} + w_{r0B}\right) - \left(w_f + w_{c1}\right)}{W_{0B}} = \frac{w_{m0B} - w_{m0}}{W_{0B}} = \Delta m_{w0B \to 1}$$

The impregnated ACC-0 BIM substrate weight changes by $W_{0B} = W_1\left(1 - \eta_{l1}\right)^{-1}$ and the original as-molded substrate changes by $W_A = W_1\left(1 - \eta_{0l}\right)^{-1}\left(1 + \eta_{go}\right)^{-1}\left(1 - \eta_{l0}\right)^{-1}$.

Recognizing that $\eta_{go} = w_{r0B}/W_{0B}$ and that the matrix of the composite at the second carbon state consists of carbonized resin from the as-molded state plus carbonized resin from ACC-0 impregnation/cure, the total weight of carbon deposit in the substrate after pyrolysis to the 1 state is:

$$w_{c1} = y w_{r0B} + w_{c0}$$

from which η_{l1} can be written as:

$$\eta_{l1} = \frac{w_{r0B} - y w_{r0B}}{W_0\left(1 + \eta_{g0}\right)} = \eta_{g0}\left(1 - y\right)\left(1 + \eta_{g0}\right)^{-1}$$

So for the composite with ACC-0 impregnation/cure weight gain of $\eta_{g0} = 12.8\%$, the expected weight loss to state 1 is $\eta_{l1} = 5.0\%$ in comparison to the table value of 5.7%

The matrix weight fraction (carbon content) at state 1 can be derived:

$$m_{w1} = c_{w1} = 1 - \frac{w_f}{W_1} = 1 - \frac{w_f}{W_{0B}\left(1 - \eta_{l1}\right)} = 1 - \frac{w_f}{W_0\left(1 + \eta_{g0}\right)\left(1 - \eta_{l1}\right)}$$

$$m_{w1} = 1 - f_{w0}\left(1 + \eta_{g0}\right)^{-1}\left(1 - \eta l1\right)^{-1}$$

$$m_{w1} = 1 - \left(1 - m_{w0}\right)\left(1 + \eta_{g0}\right)^{-1}\left(1 - \eta_{l1}\right)^{-1}$$

Using $m_{w0} = 16.5\%$, $\eta_{l0} = 11.1\%$, $\eta_{g0} = 12.8\%$ and $\eta_{l1} = 5.7\%$, we have $m_{w1} = 21.5\%$ which seems quite reasonable for the second carbon state but cannot be easliy verified.

Perhaps one of the most important parameters monitored throughout the carbon-carbon densification sequence is the quantity of carbonized resin deposited or 'carbon weight gain' due to each densification cycle. The amount of glassy carbon formed gradually decreases after each cycle and is referred to as *incremental carbon gain* while the total amount of carbon weight gained successively over the course of densification increases and is identified as *cummulative carbon gain*.

The incremental fraction of weight gain an ACC substrate experiences during each cyclic conversion from one carbon state to the next carbon state is the positive difference in substrate weight before and after each complete impregnation/cure/pyrolysis cycle divided by the former weight. Cummulative carbon gain at a subsequent state i is the positive difference in substrate weight at state i and the first carbon state 0. For the first cycle, incremental and cummulative carbon weight gain values are identical. Substrate weights used for the calculation are simply the ACC-0 panel weight (first carbon state) and the ACC-1 weight (second carbon state), so from state 0 to state 1, designated as $0 \to 1$, the fraction of carbon gained can be written:

$$\eta_{c0\to 1} = \frac{W_1 - W_0}{W_0}$$

$\eta_{c0\to 1}$ is a measure of the change in matrix weight fraction from carbon state 0 to carbon state 1:

$$\eta_{c0\to 1} = \frac{w_{c1} - w_{c0}}{W_0} = \Delta m_{w0\to 1}$$

In this case, the two matrix weights w_{c0} and w_{c1} consist entirely of amorphous glassy carbon; carbonized resin from the as-molded state, $w_{c0} = yw_{rA}$, and this weight plus carbonized impregnant resin from the first impregnation/cure, $w_{c1} = yw_{r0B} + w_{c0}$. Thus, first incremental carbon gain from the ACC-0 carbon state to ACC-1, $\eta_{c0\to 1}$ can be written in terms of the previous (ACC-0 BIM) impregnation/cure weight gain:

$$\eta_{c0\to 1} = y\,\frac{w_{r0B}}{W_0} = y\eta_{g0}$$

So for η_{g0} = 12.8% , the carbon gain after the first densification cycle from state 0 to state 1 is $\eta_{c0\to 1}$ = 7.2% as compared with the table value of 6.6%.

Repetition of the Carbon-Carbon Densification Cycle

Incremental carbon gain from state 1 to state 2 is straightforward:

$$\eta_{c1\to 2} = \frac{w_{c2} - w_{c1}}{W_1} = y\eta_{g1}$$

And incremental carbon gains for subsequent carbon states are then $\eta_{c(i-1)\to i} = y\eta_{g(i-1)}$.

Now, since the second cummulative carbon gain is defined as:

$$\eta_{c0\to 2} = \frac{W_2 - W_0}{W_0} = y\,\frac{(w_{r0B} - w_{r1B})}{W_0} = y\left(\eta_{g0} + w_{r1B}W_0^{-1}\right)$$

and

$$W_0 = W_{0B}(1 + \eta_{g0})^{-1} = W_1(1 + \eta_{g0})^{-1}(1 - \eta_{l1})^{-1}$$

then cummulative carbon gain from state 0 to state 2 is:

$$\eta_{c0\to 2} = y\left[\eta_{g0} + \eta_{g1}(1 + \eta_{g0})(1 - \eta_{l1})\right]$$

which can be written in terms of incremental carbon gains:

$$\eta_{c0\to 2} = \eta_{c0\to 1} + \eta_{c1\to 2}(1 + \eta_{g0})(1 - \eta_{l1})$$

As processing carries the substrate from one carbon state to the next, its weight changes according to impregnation gains and pyrolysis losses. The ACC-0 substrate is densified over several carbon-carbon cycles to a designated i^{th} carbon state:

$$W_0 = W_1(1+\eta_{g0})^{-1}(1-\eta_{l1})^{-1} = W_2(1+\eta_{g0})^{-1}(1-\eta_{l1})^{-1}(1+\eta_{g1})^{-1}(1-\eta_{l2})^{-1} = \text{etc...}$$

Symbolically,

$$W_0 = W_i \prod_{1}^{i} (1+\eta_{g(i-1)})^{-1}(1-\eta_{li})^{-1}$$

Or, in terms of the as-molded composite weight,

$$W_A = (1-\eta_{l0})^{-1} W_i \prod_{1}^{i} (1+\eta_{g(i-1)})^{-1}(1-\eta_{li})^{-1}$$

Also, carbonized resin is cummulatively deposited within the composite:

$$\eta_{c0\to i} = \eta_{c0\to 1} + \eta_{c1\to 2}(1+\eta_{g0})(1-\eta_{l1}) + \ldots + \eta_{c(i-1)\to i} \prod (1+\eta_{g(i-2)})(1-\eta_{l(i-1)})$$

$$\eta_{c0\to i} = \eta_{c0\to 1} + \sum_{2}^{i} \eta_{c(i-1)\to i} \prod_{2}^{i} (1+\eta_{g(i-2)})(1-\eta_{l(i-1)})$$

Finally, the matrix weight fraction at any subsequent carbon or bimatrix state i can be similarly represented:

$$m_{wi} = 1-(1-m_{w0})\prod_{1}^{i} (1+\eta_{g(i-1)})^{-1}(1-\eta_{li})^{-1}$$

Of particular interest are the matrix (carbon) weight fractions at each of the consecutive carbon-carbon states. These quantities can be estimated from the original as-molded matrix weight fraction (resin content) and subsequent substrate impregnation/cure weight gains and pyrolysis weight losses:

At ACC-0 . . . . . $m_{w0} = 1-(1-m_{wA})(1-\eta_{l0})^{-1}$

At ACC-1 . . . . . $m_{w1} = 1-(1-m_{wA})(1-\eta_{l0})^{-1}(1+\eta_{g0})^{-1}(1-\eta_{l1})^{-1}$

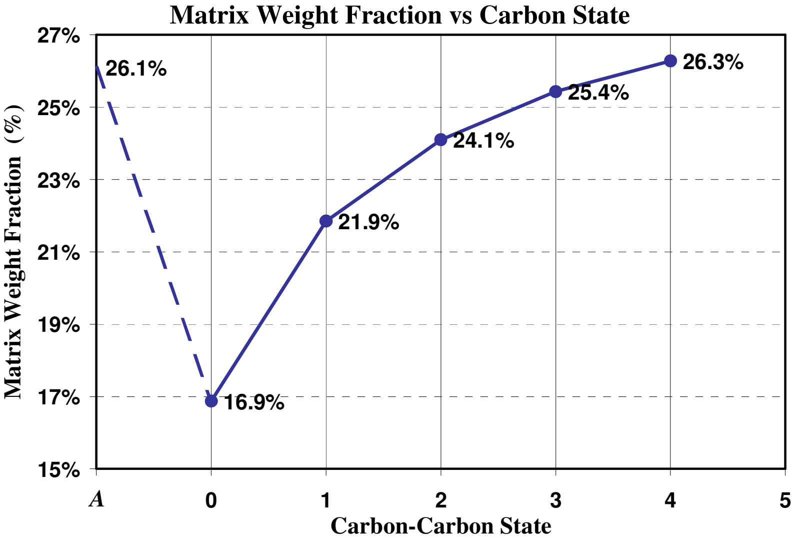
At ACC-2 . . . . . $m_{w2} = 1-(1-m_{wA})(1-\eta_{l0})^{-1}(1+\eta_{g0})^{-1}(1-\eta_{l1})^{-1}(1+\eta_{g1})^{-1}(1-\eta_{l2})^{-1}$

And so on...

Thus, with accurate measurements for initial as-molded resin content and substrate weight changes after each pyrolysis and impregnation/cure, the composite carbon matrix weight fraction can be monitored throughout the entire densification process. This property cannot be directly measured as with acid digestion techniques for composite resin content determination. It must be derived by other means. The importance of characterizing substrate matrix weight fraction is especially crucial for carbon-carbon composites since the very nature of this particular material system is based on the concept of matrix densification. It is quite plausible that precise knowledge of a composite's matrix fraction and porosity at the fully densified state are the key properties in choosing the exact process parameters to be employed for effective coating operations.

Graphical Analysis of Matrix Content and Other Parameters from the Table of Averages

Using Table of Average values for as-molded resin content, impregnation/cure weight gains, pyrolysis weight losses, and the formulas derived above, matrix weight fraction m_{wi} at each carbon state up to ACC-4 is calculated and plotted below:



Functional expressions for this plot can be acquired which describe the response of the material property (m_{wi}) as it enters and progresses through the densification process. It is postulated that the graphical behavior of m_{wi} starting with the first carbon state (ACC-0) is best represented by an exponential response function that can take either the form

$$m_{wi} = a\left(1 - e^{-bi}\right) + c \qquad \text{or its inverse . . .} \qquad m_{wi} = ae^{-bi} + c$$

While other functional forms can be made to fit the data and indeed were examined, it is felt that these representations not only provide accurate curve fits, but also reveal important information about the variable's extreme points. Using nonlinear regression analysis, precise curve fits were applied to the data utilizing these particular functional forms and the results are given below:

$m_{wi} = a\left(1 - e^{-bi}\right) + c$	$m_{wi} = ae^{-bi} + c$
Coefficient Data:	Coefficient Data:
a = 9.9431408 b = 0.66074096 c = 16.938447	a = -9.9431404 b = 0.66074107 c = 26.881587
Correlation Coefficient: 0.99937591	Correlation Coefficient: 0.99937591
When i is large, $m_{wi} \longrightarrow a + c$ = 26.9 When i is small, $m_{wi} \longrightarrow c$	When i is large, $m_{wi} \longrightarrow c$ When i is small, $m_{wi} \longrightarrow a + c$ = 16.9

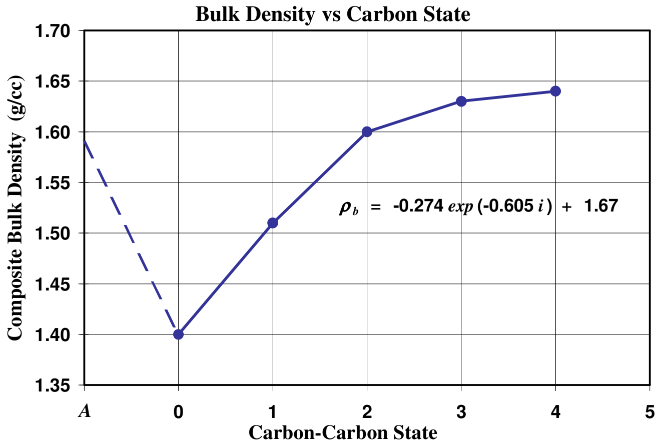
Since overall substrate averages were employed in this example, it should be realized that the particular coefficient data given here is representative only of the *average* composite article which is subjected to the densification process.

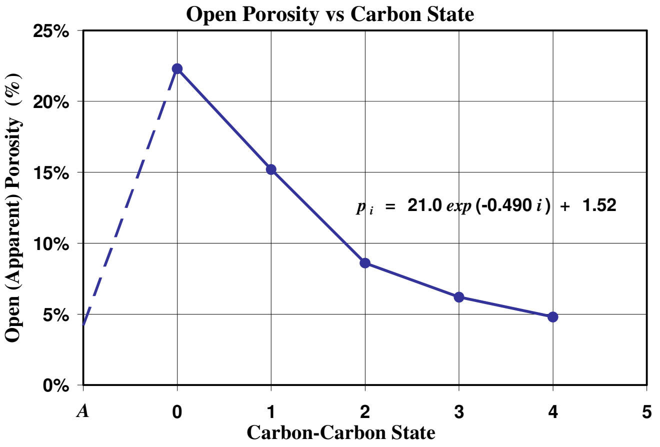
Indications reflecting the lower limit of m_{wi} are readily observed in the $m_{wi} = a\left(1 - e^{-bi}\right) + c$ expression from the value of the constant c while the $m_{wi} = ae^{-bi} + c$ form illustrates the likely value for m_{wi} if cyclic densification were carried on indefinitely. For the sake of simplicity, it will be suggested that the average % matrix by weight of typical composite substrate articles passing through the carbon-carbon densification process can be adequately represented by:

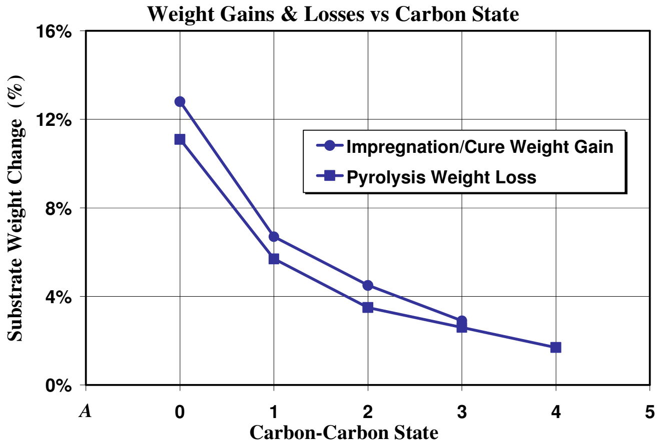
$$m_{wi} = -9.94 \; exp(-0.661\,i) + 26.9 \;\Big|_{i=0}^{\infty}$$

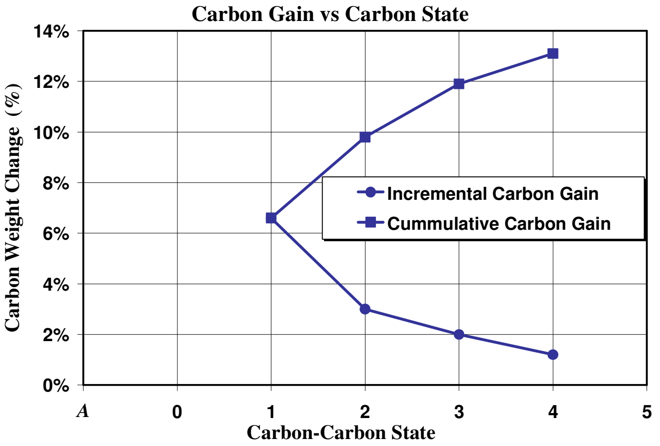
As indicated, this expression is only applicable to substrates which have undergone the first pyrolysis and have begun the densification process (after conversion from the as-molded state to the first carbon state), ie... the expression only describes the carbon-carbon densification process and says nothing about the substrate's original as-molded properties.

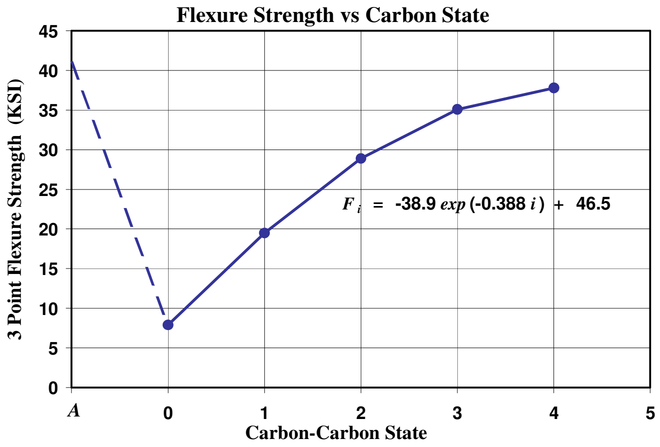
Other properties from the Table of Averages were evaluated and treated in a similar manner and their plots are given on the following page. Functional expressions for ρ_b , p , F (flexural strength) and I (interlaminar tensile or ILT strength) have been obtained and are included in each graph. In the same manner, the curve finding process consisted of evaluating a variety of nonlinear forms and concluding that the $m_{wi} = ae^{-bi} + c$ expression most appropriately represents the *average* behavior of each property as it progresses through the densification process. As with the matrix weight fraction, the dashed line from state A to the first carbon state is not represented by the relationship but is included in the graphic for illustrative purposes only.

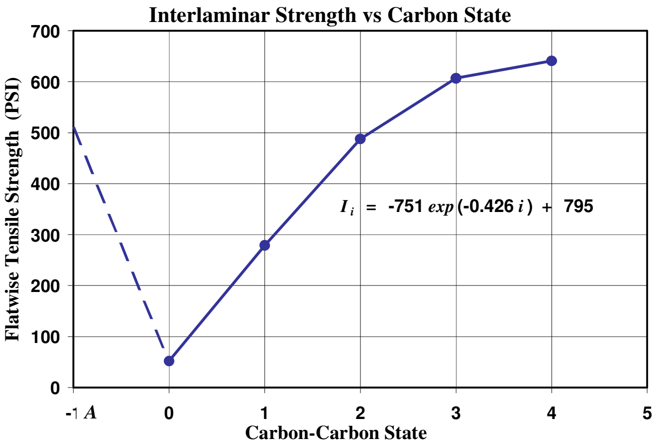












Academically, these graphical represenations are very important since they illustrate the typical behavior patterns associated with composite substrates subjected to the densification process. However, this approach does not represent material properties in the as-molded state or contain any meaningful implications for connecting the as-molded state to the first carbon state (the beginning of densification). They can only be helpful for describing articles after the first pyrolysis. In addition, the numerical expressions developed here are not specific to any particular article but are representative only of the average composite substrate pertaining to this study which underwent typical densification procedures. An attempt to develop a link between the as-molded state and subsequent densification stages is explored in the next section.

Estimation of Densified Substrate Properties from As-Molded Measurements

On the average, it may be possible to make approximations and quantitatively predict values for ACC-4 densified substrate from as-molded properties. Utilizing only two commonly measured as-molded parameters (resin content m_{wA} and bulk density ρ_{bA}) along with some of the expressions and constants introduced earlier in the discussion, a so-called *model* can be developed which provides rough estimations for some of the relevant material properties at each of the successive carbon states. Again most of the formulas required for this endeavor have already been developed but will be re-introduced here or developed as necessary.

Initial pyrolysis of the as-molded article (pyrolytic conversion to the first carbon state ACC-0) has already been defined in terms of the resin content and the constant y (phenolic resin char yield).

$$\eta_{l0} = m_{wA}(1 - y)$$

Matrix weight fraction (carbon content) at the ACC-0 state was also defined earlier in similar terms:

$$m_{w0} = 1 - (1 - m_{mA})[1 - m_{wA}(1 - y)]^{-1}$$

$$m_{w0} = 1 - (1 - m_{mA})(1 - \eta_{l0})^{-1}$$

Composite bulk density at the ACC-0 state can be developed from η_{l0} by using the following scenario. It is historically documented that dimensional changes in laminate length and width are infinitesimal. They are quite insignificant and essentially impossible to measure. However, a small thickness decrease from pyrolysis of the original as-molded article generally occurs, but substrate thickness over the course of densification from ACC-0 to ACC-4 is small enough to be considered insignificant, on the average. Thickness deceases from initial pyrolysis for the Densification Studies as well as most of the articles processed in the LESS program have been found to center around a tight average of 1.67%. Thus, if we let the panel thickness in mil/ply be represented by M, then

$$\eta_{l0} = 1 - \frac{W_0}{W_A} = 1 - \frac{\rho_{b0}V_0}{\rho_{bA}V_A} = 1 - \frac{\rho_{b0}M_0}{\rho_{bA}M_A}$$

now since $\frac{M_A - M_0}{M_A} \cong 1.67\%$

then $\frac{M_A}{M_0} \cong 1.017$

and

$$\rho_{b0} = \rho_{bA}\frac{M_A}{M_0}(1 - \eta_{l0})$$

$$\rho_{b0} = 1.017\rho_{bA}(1 - \eta_{l0})$$

The fiber volume fraction was described earlier in terms of the matrix weight fraction and bulk density. Since changes in substrate length and width are ignored throughout the process and relevant thickness changes occur only from the initial pyrolysis, fiber volume fraction for the as-molded state will be estimated along with the value for ACC-0, the ladder of which then applies to all subsequent carbon states:

$$f_{v0} = (1 - m_{w0})\rho_{b0}\rho_f^{-1}$$

Apparent (open) porosity at ACC-0 can be estimated by rearranging an expression given near the beginning of the report in terms of ρ_{b0} , m_{w0} , and the two constituent densities ρ_f and ρ_c :

$$p_0 = 1 - \rho_{b0}\left[(1 - m_{w0})\rho_f^{-1} + m_{w0}\rho_c^{-1}\right]$$

Bimatrix weight gain at the ACC-0 state was derived earlier using a hypothetical equivalency between the open porosity and the imprenating resin resulting in:

$$\eta_{g0} = s p_0 \rho_r' \rho_{b0}^{-1}$$

An expression for a second impregnation/cure at ACC-0 was also developed but will not be considered here since most of the articles treated in this study underwent single impregnation/cure cycles exclusively.

Pyrolysis weight loss of the ACC-0 BIM article to ACC-1 was described earlier and is given below:

$$\eta_{l1} = \eta_{g0}(1 - y)(1 + \eta_{g0})^{-1}$$

Using analogous expressions for each subsequent carbon state through ACC-4, values can be estimated far downstream for the various properties when only the initial as-molded resin content and substrate bulk density are known, thus providing a connection route between common autoclave cured articles and fully densified ACC substrate. Utilizing the measured values for average as-molded resin content and average as-molded geometrical density from the Table of Averages (26.1% and 1.59g/cm^3 respectively), results from this approach are given in the following table.

Table of Estimated Parameters for Average Densified Substrate

Physical Property			Carbon State i				
	Unit	Symbol	0	1	2	3	4
Weight Loss from Pyrolysis to i	%	η_l	11.5	4.5	3.0	2.1	1.4
Matrix Weight Fraction at i	%	m_w	16.5	21.5	24.6	26.7	28.0
Geometrical Bulk Density at i	g/cm^3	ρ_b	1.43	1.52	1.59	1.63	1.66
Fiber Volume Fraction at i	%	f_v	62.6	-----	-----	-----	-----
Apparent (Open) Porosity at i	%	p	20.9	14.5	10.1	7.0	4.9
Weight Gain from Impreg/Cure at i	%	η_g	11.4	7.4	5.0	3.4	-----

m_{wA} = 26.1% Average as-molded resin content determined by acid digestion

ρ_{bA} = 1.59g/cm^3 Average as-molded geometrical bulk density determined by weights and measures

f_{vA} = 61.5% Average as-molded fiber volume fraction estimated from m_{wA} and ρ_{bA}

Constants: y = 56% s = 72% ρ_f = 1.91g/cm^3 ρ_r' = 1.08g/cm^3 ρ_r = 1.24g/cm^3 ρ_c = 1.43g/cm^3

Application of concepts developed from this study will be extended to future projects in order to better understand the nature of composite fabrication and carbon-carbon processing. Most importantly, it is hoped that these efforts will enhance the effectiveness of subsequent coating operations which are required to transform the carbon-carbon substrate into an oxidation protective material system for advanced aerospace applications.