NONDESTRUCTIVE EVALUATION OF CHANGES IN MECHANICAL PROPERTIES IN CARBON-CARBON COMPOSITES DURING PROCESSING

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INTRODUCTION

In the next decade, there will be a concerted effort to develop hypersonic aircraft for commercial applications. It is anticipated that the design of these vehicles will place new demands on material performance at elevated temperatures. Temperatures in excess of 3200° F will be experienced at hypersonic speeds in certain critical areas of the structure, such as the tip of the nose and the wing leading edges. Carbon-carbon composites are one of the few structural materials available which retain a significant fraction of their specific stiffness and strength at elevated temperatures. Consequently, there is a great deal of interest in carbon-carbon composites as structural materials for hypersonic applications. While this material offers much promise for the future, many problems remain to be solved before it can be effectively utilized.

One of the most important considerations in carbon-development is the effect of processing on the microstructure of the final product. Carbon-carbon composites are fabricated in a complicated, multistep process. Initially, a composite panel (called the mold panel in this study) is fabricated using conventional processing techniques. The matrix of this precursor composite is a phenolic resin and graphite fibers are used as reinforcement. This material is then exposed to elevated temperature to convert the resin to pure carbon. Naturally, this is a material with very high porosity and poor material properties ($P_0$ sample). To improve this situation, the panel is then reinfiltrated with resin (either as liquid or gas) and returned to elevated temperature for conversion of the new resin into carbon ($P_1$ sample). As this process is somewhat inefficient in filling the sample pores, it must be repeated several times ($P_2$, $P_3$, etc.) until a part with reasonable microstructural uniformity is obtained. Clearly, the properties of the final composite are heavily dependent on the efficiency of the pore filling process.
In this research effort, we examine the use of quantitative, nondestructive testing techniques to track changes in the properties of carbon-carbon composites during processing. Here, we use a combined radiography/ultrasonic velocity approach to characterize the behavior of the composite on a local basis. As wave speed is a function of both moduli and density, both nondestructive evaluation techniques are needed for accurate moduli reconstruction in a porous media such as carbon-carbon. In order to demonstrate the validity of the approach, we compare our results with direct mechanical property measurements as well as photomicrographs of the specimen microstructure taken at various stages of processing.

BACKGROUND

A variety of ultrasonic test techniques have been developed for quantitative characterization of the mechanical properties of composite media. Much of the early work in this area involved sectioning of the composite to generate the required waves for elastic moduli reconstruction (1). However, the value of using nondestructive, oblique incidence ultrasonic techniques for this determination was also recognized (2). More recently, a plethora of approaches have emerged based on bulk wave slowness surface reconstruction (3), point source-point sensor techniques (4), surface wave analysis (5), critical angle measurements (6), and plate wave propagation—the so-called leaky-Lamb wave method (7) in addition to bulk wave measurements. The key requirement for any viable NDE application of any of these approaches is the capability for rapid, local property determination so large scale parts can be scanned in a timely fashion.

While many of these approaches have been developed for conventional laminated composites, relatively little work in this area has been done on carbon-carbon materials. The one major exception to this observation is the work of Hosten and Tittman (8), who examined the effect of processing on the elastic moduli of woven carbon-carbon composite samples. Even though these researchers examined only a limited number of moduli in the orthotropic composite, the authors clearly demonstrate the viability of modulus reconstruction technique to study processing induced changes in the composite.

THEORY

The governing equations for wave propagation in anisotropic media are relatively straightforward. Assuming plane wave propagation of the form

\[ u_j = A_e \alpha_j e^{(k_x x_1 - \omega t)} \]  


the equations of motion reduce to the following eigenvalue problem

\[ \begin{bmatrix} \lambda \hat{I} - I \end{bmatrix} \alpha = 0 \] 

where

\[ \lambda_{ik} = C_{ijkl} m_i m_j / \rho \]

\[ I = \text{identity matrix} \]

\[ \rho = \text{density} \]

\[ m = \xi / v = \text{slowness vector} \]
\( \mathbf{f} \) = wave normal direction cosines

\( k \) = wave number

\( V \) = phase velocity

\( \alpha \) = direction cosines of particle displacements

\( C_{ijkl} \) = elastic-stiffness tensor

For material property characterization, we are particularly interested in velocity. In any given direction \( (\mathbf{f}) \), velocity will be a function of the moduli and density. If a sufficient number of independent velocities can be measured, there will in principle be sufficient equations to determine each of the elastic moduli. For an orthotropic media, nine moduli are sought.

To take optimal advantage of material symmetry we start by measuring the through thickness transit time which gives the corresponding modulus \( C_{33} \), directly, that is at normal incidence we have (measurement \#1) -

\[
C_{33} = \rho V^2
\]

this yields \( C_{33} \), which we use in all of our subsequent equations. Three subsequent measurements are done at oblique incidence in the radial directions \( (\phi = 0^\circ) \), measurements \#2, \#3, \#4) -

\[
\begin{bmatrix}
C_{11}\sin^2\theta + C_{55}\cos^2\theta - \rho V^2 & 0 & (C_{13} + C_{55})\sin\theta\cos\theta \\
0 & C_{66}\sin^2\theta + C_{44}\cos^2\theta - \rho V^2 & 0 \\
(C_{13} + C_{55})\sin\theta\cos\theta & 0 & C_{55}\sin^2\theta + C_{33}\cos^2\theta - \rho V^2
\end{bmatrix} = 0
\]

(4)

where measurement \#2 is for the quasi-longitudinal wave at \( \theta_{in} = 5^\circ \), measurement \#3 is for the quasi-transverse wave at \( \theta_{in} = 15^\circ \) and measurement \#4 is again for the quasi-transverse wave at \( \theta_{in} = 20^\circ \). This yields \( C_{13}, C_{11}, \) and \( C_{55} \).

Similarly measurements \#5, \#6, and \#7 are done in the tangential direction \( (\varphi = 90^\circ) \), for the same set of angles of incidence.

\[
\begin{bmatrix}
C_{22}\sin^2\theta + C_{44}\cos^2\theta - \rho V^2 & 0 & (C_{23} + C_{44})\sin\theta\cos\theta \\
0 & C_{66}\sin^2\theta + C_{55}\cos^2\theta - \rho V^2 & 0 \\
(C_{23} + C_{44})\sin\theta\cos\theta & 0 & C_{44}\sin^2\theta + C_{33}\cos^2\theta - \rho V^2
\end{bmatrix} = 0
\]

(5)

This yields \( C_{23}, C_{22}, \) and \( C_{44} \).

The final two measurements (#8, #9) are carried out at \( \varphi = 45^\circ \) because the computations simplify considerable, for oblique angles of incidence of \( \theta_{in} = 15^\circ \) and \( \theta_{in} = 20^\circ \) producing quasi-transverse waves.
\[
\begin{bmatrix}
C_{11}'\sin^2\theta + C_{33}'\cos^2\theta - \rho V^2 & C_{16}'\sin^2\theta + C_{44}'\cos^2\theta & (C_{13}' + C_{35}')\sin\theta\cos\theta \\
C_{16}'\sin^2\theta + C_{44}'\cos^2\theta & C_{66}'\sin^2\cos^2\theta + C_{44}'\cos^2\theta - \rho V^2 & (C_{36}' + C_{45}')\sin\theta\cos\theta \\
(C_{13}' + C_{23}')\sin\theta\cos\theta & (C_{36}' + C_{45}')\sin\theta\cos\theta & C_{55}'\sin^2\theta + C_{33}'\cos^2\theta - \rho V^2
\end{bmatrix} = 0 \tag{6}
\]

where

\[
C_{11}' = C_{11}\cos^4\phi + 2(C_{12} + 2C_{66})\sin^2\phi\cos^2\phi + C_{22}\sin^4\phi
\]

\[
C_{16}' = C_{13}\cos^2\phi + C_{23}\sin^2\phi
\]

\[
C_{33}' = C_{33}
\]

\[
C_{36}' = (C_{23} - C_{13})\cos\phi\sin\phi
\]

\[
C_{44}' = C_{44}\cos^2\phi + C_{55}\sin^2\phi
\]

\[
C_{45}' = (C_{44} - C_{55})\cos\phi\sin\phi
\]

\[
C_{55}' = C_{44}\sin^2\phi + C_{55}\cos^2\phi
\]

\[
C_{66}' = C_{66}\cos^2\phi + (C_{11} - 2C_{12} + C_{22})\cos^2\phi\sin^2\phi
\]

which yields \( C_{12} \) and \( C_{66} \).

Also, it should be pointed out that, in anisotropic media, the phase and group velocities do not coincide. Since group (not phase) velocity is the quantity being measured, we employ the group velocity formulation of the above problem.

\[
S_q = \frac{C_{ijkl}\alpha_k\alpha_l}{\rho V^2}
\]

where \(|S| = v_{\text{group}}\)

A commercially available numerical analysis code (IMSL) was used to solve the resulting set of coupled nonlinear equations for the desired moduli.

**EXPERIMENTAL PROCEDURE**

We studied a series of C-C test panels to investigate the effects of processing on material properties. The processing of these samples was stopped at different stages in the manufacture in order to examine the effectiveness of the reinfiltration process. The experimental approach to characterizing C-C microstructure was principally based on ultrasonic velocity measurements. However, since ultrasonic velocity measurements are sensitive to both elastic moduli and density in order to characterize the elastic anisotropy, it was necessary to have an additional local measure of density. In this case, radiographic tests methods were employed for this purpose.
The experimental setup is shown in Figure 1. In order to prevent moisture absorption during the inspection process, the samples were sprayed with an acrylic coating layer. The layer was sufficiently thin that it can be safely neglected in the time-delay measurements. A test fixture instrumented with an RVDT for accurate angular positions was used for pulse-echo inspection at fixed angles of incidence. The parts were scanned in a raster mode. In order to increase sensitivity to small changes in local material properties, a pulse phase locked loop circuit was employed.

Radiographic test methods were used for local density determination in the composite samples. For this measurement, radiographs of the complete parts were made along with an x-ray image of an aluminum calibration bar (stepped in increments of 0.05 inch). Then, we converted the photographic x-ray images to digital form. This was done using a digitizing camera. By comparing the C-C calibration block to the A1 sample, the absorption coefficient for C-C is then directly established. This permits local density measurements.

RESULTS and DISCUSSION

Ultrasonic testing was then used to determine the 9 pertinent elastic moduli for the orthotopic samples. Results were then compared with mechanical test results for coupon cut from the plates. Average porosity was also determined for each sample plate. Results are presented in Figure 2. As expected, the average porosity was found to increase dramatically with the first pyrolyzation and then slowly decrease with successive densifications. We also studied changes in pore size with processing. Figure 3 shows that the successive densifications of the manufacturing process preferentially fill the 0.3- to 10-micrometer-sized pores and that large pores do not fill well.

To examine this further, representative photo micrographs were obtained for each of the sample densifications. Several major microstructural defects are found in the micrographs: matrix porosity (principally seen at fiber crossing points), fiber-matrix debonding (probably due to the mismatch in the thermal expansion coefficients of fiber and matrix) and matrix microcracking. As seen in the photomicrographs, large scale porosity

![Fig. 1 Experimental geometry.](image-url)
is only reduced slightly by successive reinfiltrations. By the final step, the small scale porosity and matrix microcracking are reduced substantially from that of the $P_0$ state, but not eliminated. Furthermore, fiber matrix debonding which was virtually complete throughout the specimen in the $P_0$ state, is also improved by the $P_5$ densification, but also not completely eliminated.

For the ultrasonic method to be meaningful, the mechanical test values, although obtained from multiple test coupons spread out over the surface of the six sample panels, should be representative of the values obtained by the ultrasonic wave velocity analysis. The data shown in Figure 4 exhibit the relationship between the compressive test and ultrasonic stiffness values for selected moduli. The upper and lower ultrasonic stiffness values are shown on the graphs so that the entire range of stiffness values obtained over the sample panel’s surface may be represented in the comparison.

Three important observations may be made from these data. The first is that for each of the seven stiffness coefficients investigated, the mechanical test values were within the high-low spread of ultrasonic test values. This clearly implies that the ultrasonic stiffness values were reliable predictions of the material stiffness. The one exception was the $P_6$ panel in which the mechanical test values were either at the low end or out of range of the ultrasonic stiffness values. This anomaly in the accuracy of the ultrasonic method may best be explained by the high void-porosity value found in the $P_0$ panel.
The second observation that may be made from the comparison graphs is that
the standard deviation of the ultrasonic stiffness values (with the exception of the initial $P_0$
sample) decreases with processing, indicating a more uniform microstructure. The
standard deviation of the ultrasonic test values increased from the initial mold/cure state to the
$P_0$ state and then decreased with successive densifications ($P_1$ through $P_5$). This trend
in the standard deviation value follows the tendency of the void-porosity value with
successive densification; thus, the manufacturing process tends to decrease the property
variations found through the material.

![Fig. 4](image)

**Fig. 4** Effect of processing on elastic moduli: a) $C_{11}$, b) $C_{33}$, c) $C_{12}$.

The third observation is the effect of the manufacturing process (densification)
on the individual stiffness components. As observed in the mechanical test results, the
ultrasonic stiffness values generally decreased with the first pyrolysis and then
increased with each successive densification. This is again a result of the manufacturing
process. Clearly, considerable damage, hence material property degradation, is
introduced into the sample during the initial processing stage ($P_0$); of particular interest
is the observation that this effect is most prominent for the matrix-dominated properties.
For example, the normal stiffness in two fiber directions $C_{11}$ and $C_{22}$ are only reduced
to about 20% from their initial (phenolic composite) value, while the through-thickness
normal stiffness is reduced to 25% of its initial value. Thus, even though the fibers are
almost completely debonded from the matrix, there is only a marginal reduction in the
normal stiffness (in-plane) as the matrix carries very little of the load. For moduli which
depend heavily on the transfer of load between fiber and matrix, the reduction is
significantly more pronounced. One modulus $C_{12}$ was actually found to be stiffer after
the initial processing stage. This is a Poisson-type term in the plane of material
reinforcement. This modulus was found to decrease with increasing densification. We
also find that the normal and shear stiffness as well was, by the end of the last
processing stage, were all higher than the values for the original matrix, possibly due to
the increased stiffness of the matrix. The two remaining moduli $C_{13}$ and $C_{23}$ never
returned to their original values. Also, the behavior of these moduli seemed to be
asymptotic with processing. Hence, we doubt that further processing will markedly
influence the overall composite stiffness. Finally it should be noted that these results
apply to stiffnesses, not strength. The large scale defect structure introduced by
processing and conversion of the matrix to less ductile carbon means that strength
reduction is to be expected.
CONCLUSIONS

Quantitative nondestructive test techniques have been used to study the effects of processing on the mechanical behavior of carbon-carbon composites.

Most of the elastic moduli (stiffnesses) were found to decrease after the first pyrolyzation and increase thereafter. In many cases the stiffness values in the final state were higher than they were in the precursor composite. Poisson type terms \((C_{12}, C_{13}, C_{23})\) behaved in an opposite fashion. The degree of material inhomogeneity was found to decrease with each processing stage.

Results were compared with direct mechanical property measurements, good agreement was observed.

A photomicrographic study of changes in material microstructure was also completed. While overall sample porosity decreased with processing, small scale pores were found to fill preferentially. Also, matrix microcracks were not found to fill efficiently in the impregnation/pyrolyzation process.

From these observations, we conclude that the increase in stiffness with processing is attributable to the increased stiffness of the carbon matrix over its polymer precursor. We also believe that part quality would be considerably increased if a more uniform pore size distribution could be achieved in the initial pyrolyzation.

REFERENCES