

ONE-STEP DENSIFICATION OF CARBON/CARBON COMPOSITES: IS IT FEASIBLE?

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Introduction

With the increased emphasis on lower-cost production of carbon/carbon (C/C) composites, more attention is being directed toward lower-cost fibers and the use of very high char-yield resins and pitches as impregnants. This paper deals with the latter subject, and stresses that high char yield has in some circles become a "red herring" in as much as it is only one of a number of important variables to consider in densification, and, more specifically, as the author discussed previously,¹ it is the volume yield rather than the mass yield of impregnant, following pyrolysis and subsequent heat treatment, that is the key parameter in assessing densification efficiency for liquid-phase densification. This should be intuitively obvious since the goal of all composite densification is to fill void space. However, as will be shown, volume densification yield alone is not sufficient to evaluate overall densification efficiency, and other factors such as dimensional change of the composite in response to dimensional change of the matrix with heat-treatment temperature (HTT), fiber-matrix adhesion, and impregnant viscosity as it influences initial impregnant infiltration must also be taken into account. Furthermore, the properties of C/Cs are influenced by these factors, and careful thought should also be given to the tradeoffs between properties, porosity, and carbon microstructure as influenced by impregnant type and HTT.

Results and Discussion

The volume densification yield is defined¹ for a unit volume of composite as

$$\Delta V/\theta = Y_m \rho_0/\rho_1, \quad (1)$$

where ΔV is volume fraction of carbon matrix "deposited" in the available composite volume fraction porosity, θ ($= 1 - V_f$ prior to first densification), Y_m is the mass yield of impregnant, ρ_0 is the density of the starting resin or pitch, and ρ_1 is the density of the carbon matrix at the particular HTT employed. It is assumed that the initial infiltration of resin or pitch impregnant is 100% efficient. It can be seen that even for a char yield of 100%, the efficiency with which the matrix porosity is filled is significantly limited by the density ratio, ρ_0/ρ_1 . As a practical example, consider a pitch with a char yield of 90% (as can be realized by using ~5000 psi pressure during pyrolysis). The density of pitches is typically about 1.35 g/cm³, and if heat treated to typical graphitization HTTs, the carbon matrix density ρ_1 will be about 2.2 g/cm³. Using Eq. (1), we calculate for these conditions a maximum volume densification yield of only 55%. For a C/C with $V_f = 0.60$, the residual porosity following this first cycle would be at least 18%. From Eq. (1), we see that if ρ_1 could be reduced, the volume yield would increase proportionately. However, to achieve this with a coal-tar or petroleum pitch would require using lower HTTs since for soft carbons, density is a mono-

tonically increasing function of HTT. This brings us to the issue of tradeoffs in mechanical and thermal properties. If we are seeking high thermal conductivity, then a high HTT ($> 2500^\circ\text{C}$) is necessary. And if we are to avoid forming a brittle-matrix composite, a high HTT is again required. Similarly, if our concern is minimizing ablation in a rocket nozzle throat, high matrix density is again a requirement.

For the case of thermosetting resin-matrix precursors, *real* density is not a simple function of HTT. Figure 1 illustrates this for phenolic resin ($Y_m = 0.62$) and a high-char-yield polyarylacetylene (PAA) resin ($Y_m = 0.90$). The results are taken from Ref. 2. Note the large drop in density for the PAA-derived matrix near 1800°C HTT. Such density minima are typical of hard carbons.³ Clearly, if one were only concerned with volume yield, an 1800°C HTT for PAA would give the highest value. With phenolic resin, there is no pronounced density minimum, and the best yield would be realized using a HTT of ~1000–1800°C. Following 1800°C HTT, the densities of both resins rise sharply. This is due primarily to stress graphitization of the matrix.⁴ Since the results shown in Fig. 1 were obtained from unidirectional fiber tow composites, the densities represent an upper bound of in-situ matrix composite densities since, in a single tow, a high fraction of the matrix is relatively close to the fibers, which, as shown elsewhere,⁴ is the principal factor influencing the extent of stress graphitization of the matrix. In 2-D and 3-D composites, there would be relatively large interstices between fiber bundles, and in these regions there is significantly less stress graphitization. This would result in a lower average matrix density at higher HTTs than shown in Fig. 1.

The above discussion does not take into account the effects of composite consolidation, which can occur when the matrix shrinks during pyrolysis. In order for this to be a significant factor in eliminating porosity, the composite must have at least one unreinforced direction, and there must be good adhesion between fiber and matrix. The application of a compaction pressure in the unreinforced direction also assists in consolidation. In 3-D C/Cs, for example, the fibers restrain composite shrinkage in all directions, and densification of 3-Ds is simply a matter of volume densification yield. At the other extreme, 1-D single tows are mechanically uncomplicated, and, as a rule, the (negative) dimensional change of the tow will be approximately that of the matrix, and the final heat-treated C/C tow will frequently have negligible porosity. Of more practical interest are 2-D composites, which can shrink in the thru-thickness (unreinforced) direction. We can combine composite consolidation with volume densification yield to define an overall densification efficiency, E , which can be expressed as

$$E = \frac{\Delta V_m}{\theta} - \frac{\Delta V_c}{\theta} = \frac{\Delta V_m - \Delta V_c}{\theta}, \quad (2)$$

where the only new term to be defined is ΔV_c , which is the change in volume of a composite of initial unit (bulk) volume. As written in Eq. (2), ΔV_c can be either negative (shrinkage) or

positive (expansion). Matrix expansion is, of course, the exception, but has been observed¹ in 3-D C/Cs following high HTTs at high composite densities. This phenomenon of "billet growth" is the result of irreversible opening of microcracks in the matrix. We would expect to see this in 2-D C/Cs as well. Therefore, we see that the HTT needs to be evaluated carefully since, for a given matrix, it can be optimized to give maximum densification efficiency by minimizing both ρ_1 and the extent of matrix microcracking.

Using the resin data from Fig. 1 and the pitch data from Ref. 1, Fig. 2 has been constructed to illustrate the points discussed above. Both E and residual porosity are plotted following one densification cycle for 1-D single tow, and 2-D and 3-D C/C composites as a function of impregnant volume yield. That is, with the exception of the 1-D tows where nearly full consolidation is assumed, the points plotted for 2-Ds are values of volume yields calculated for the two resin impregnants at the given HTTs, i.e., they represent lower bounds for E. For 3-D structures, the range of pitch volume yields is shown from a low of about 0.15 for a completely dry preform to a high of about 0.52. The source of this data, taken from Ref 1. For illustrative purposes, E and θ are also plotted for a hypothetical densification using PAA at its maximum volume yield of about 0.72, corresponding to $\rho_1 \sim 1.4 \text{ g/cm}^3$ and an HTT $\sim 1800^\circ\text{C}$.

For the 2-D structures, the vertical distance between plotted points and the ordinate value of $E = 1.0$ is a measure of the maximum possible composite consolidation. In addition to the importance of the already-mentioned fiber-matrix adhesion, the type of fabric (e.g., square weave, 8-harness satin, etc.) and method of lay-up and resin cure would also be expected to influence the extent of consolidation. There is a serious need for reliable data on this subject.

Conclusions

It has been argued that in order to produce an acceptable C/C composite in one cycle of densification, careful thought must be given to matrix properties—in particular, the volume densification yield, which is a function of the char yield, the resin density, and the carbonized matrix density which, in turn, is a function of HTT. In addition, for 1-D and 2-D structures, composite consolidation resulting from resin shrinkage during pyrolysis can improve overall densification efficiency. Factors such as fiber-matrix adhesion, fabric type, and lay-up and cure procedures can play an important role in consolidation. The bottom line comes down to two simple questions that the user/manufacture must ask: (1) What is an acceptable level of porosity consistent with the desired mechanical properties? (Porosity is particularly significant in affecting matrix-dominated properties such as a cross-ply tension and interlaminar shear.) (2) For a given porosity, what combination of matrix and HTT will provide the appropriate carbon microstructure that will yield the desired mechanical and/or thermal properties?

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References

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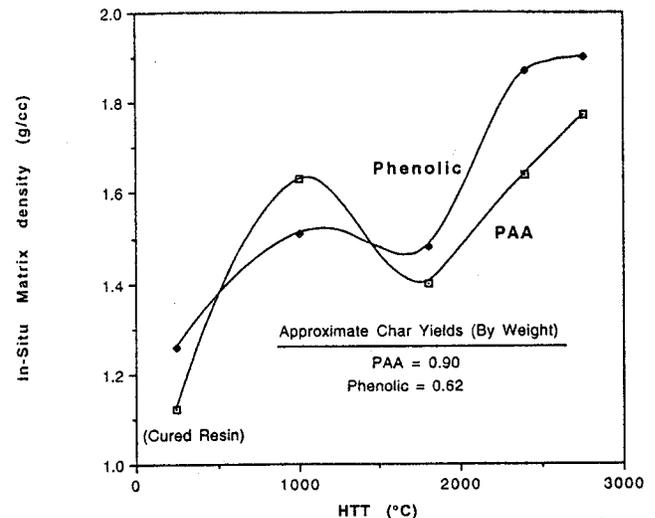


Figure 1. In-situ matrix density vs HTT (Data from Ref. 2).

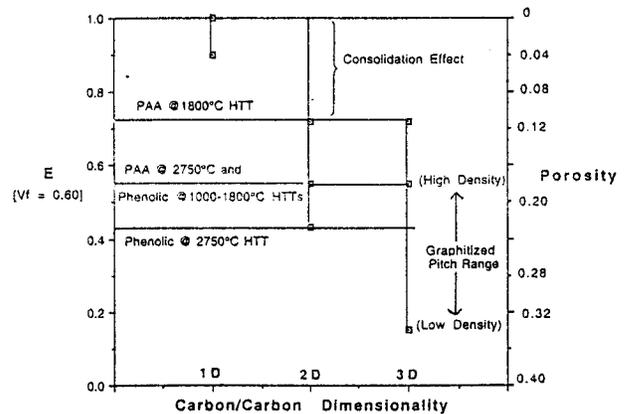


Figure 2. Densification efficiency, E, and porosity for 1-D (single tows), 2-D, and 3-D C/Cs after one densification cycle for different impregnants and HTTs. For 2-Ds, points are volumetric yields with no composite consolidation, and vertical distance between points and ordinate value $E = 1$ reflect effect of composite consolidation.