Effects of amount, location, and character of porosity on stiffness and strength of ceramic fiber composites via different processing

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The porosity dependence of ceramic fiber composite Young's modulus, and especially tensile strengths, is reviewed. Though limited, data shows markedly different porosity dependencies for composite matrices derived from: (1) chemical vapor infiltration (CVI), (2) preceramic polymer pyrolysis, or (3) hot pressing of powders. CVI results in initially limited, then accelerating, rates of property decreases as porosity increases, as for typical monolithic ceramics. In contrast, hot pressing and polymer pyrolysis result in the opposite behavior, i.e., high initial then diminishing rates of property decreases. This markedly differing behavior is attributed to pores being rounded and especially away from the fiber-matrix interfaces in CVI while in hot pressing and polymer pyrolysis fiber-matrix interface, cusp/lenticularshaped pores (more difficult to remove and dominant at lower porosity levels) are more detrimental to properties, similar to grain boundary pores in monolithic ceramics. Competition between such interfacial pores and those totally in the matrix in both their elimination and the effects of those pores remaining in the processed composite is consistent with data differences and scatter. Implications for properties achievable by the above 3 types of processing, as well as for sintering of composites and possible use of porous layers at the fiber-matrix interface to limit oxidative embrittlement are noted. © *1999 Kluwer Academic Publishers*

1. Introduction

Ceramic fiber composites have become of substantial interest because of their high degree of resistance to crack propagation, especially catastrophic failure. Effects of porosity on properties of such composites have been studied very little, in part since such bodies are often hot pressed to yield little or no porosity, hence high property levels. However, porosity effects are important since some porosity often remains from hot pressing, and is typically substantial when composites are sintered. Further, considerable porosity is also commonly left in making composites by using preceramic polymers as the matrix source, or making composites by chemical vapor infiltration (CVI). Additionally, composite porosity may be important since use of porous layers around fibers has been proposed as a means to inhibit oxidative embrittlement as a result of composite exposure to high temperatures under oxidizing conditions.

This note addresses the issue of the effects of the amount and character (hence also location) of porosity on Young's modulus and especially tensile/flexure strength of various ceramic fiber composites made by hot pressing, CVI, and via preceramic polymers as the matrix source, with all but the CVI composites being exclusively uniaxial composites tested with the stress parallel to the fiber axis. This note is derived from two surveys of composite properties [1, 2] and is published separately here to present the combined results in a more comprehensive fashion and to further call attention to important implications of these results.

2. Data presentation and discussion

First consider CVI SiC composites, where both Young's modulus [2, 3] and flexural [1–6] strength versus porosity have been obtained over a substantial range of porosity, especially for strength for the same or similar composites. Thus, Young's modulus shows modest decreases with increasing porosity that is essentially linear on a semilog plot (Fig. 1), as previously reviewed [2]. The decrease in the moderate to intermediate porosity range gives a semilog slope (b value) of ~3, i.e., giving the ratio of Young's modulus at any volume fraction porosity (P) to that at $P = 0$, i.e., E_0, as e^{-3P}. This porosity correction is in the normal, more modest, range encountered for ceramics and other materials with nominally spherical pores [1, 7, 8].

Next consider flexural strength data for the same and similar SiC CVI composites [3–6], as well as various composites with SiC-based (Nicalon) fibers that were hot pressed with different crystalline ceramic matrices to differing levels of porosity during evaluation and development studies (Fig. 2) [1, 9]. Data from a summary evaluation of the behavior of hot pressed composites using a silicate-based glass matrix with carbon fibers
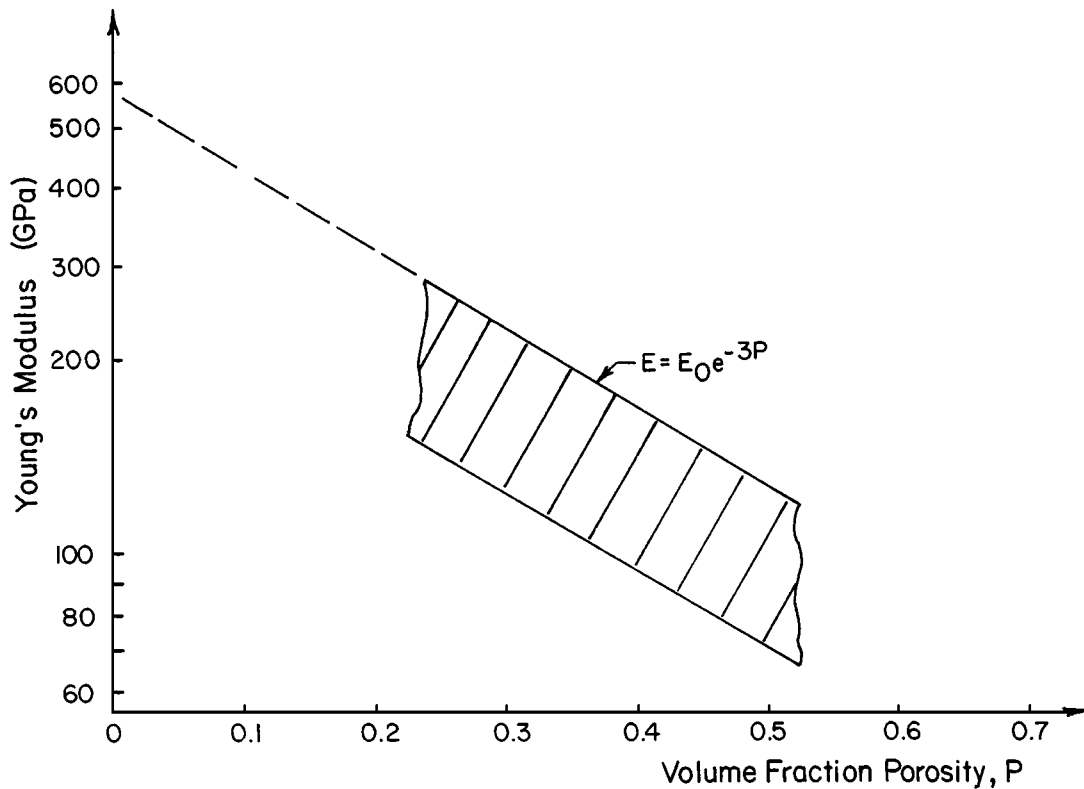
Figure 1 Semilog plot of Young' modulus versus volume fraction porosity (P) at 22 °C for SiC fiber composites made by CVI [2, 3]. Published with permission of Technomic Press.
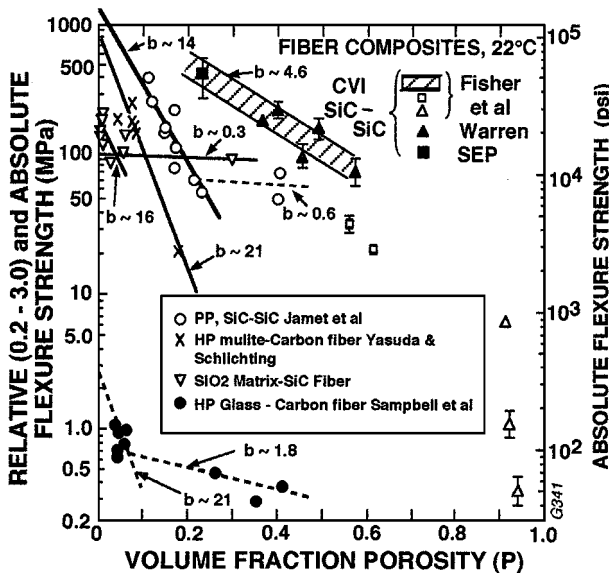

Figure 2 Flexural strength at 22 °C for ceramic fiber composites with matrices obtained from CVI [1–6], hot pressing (HP) [1, 9–11], and polymer pyrolysis (PP) [12]. (Data for glass matrices is in terms of relative values, which exceed 1 due to using 'theoretical' strengths to allow use of data of differing fiber contents [10, 11].) Note the not uncommon somewhat higher *b* value for strength versus Young's modulus for the CVI composites (Fig. 1) and the clear overall consistency with the trends for MSA models [1, 7, 8] (including a high P_C value consistent with the modest *b* values), and the bilinear character of the PP [12] and the HP-SiO$_2$ glass matrix composites [9], and the similarity of these to other data as discussed in the text. Published with permission of Marcel Dekker.

is also included [1, 10, 11]. This entails a normalization used by the original authors to increase the limited amount of data to compare composites with differing levels of fiber contents and porosity (leading to nor-

malized strengths substantially >1). Additionally, data from an experimental study of using a preceramic polymer to produce a SiC matrix, again with the same SiC-based fibers [1, 12] also provides data as a function of P. All of this data is presented as a semilog plot of strength versus P (Fig. 2). Though much of the non-CVI composite data is limited, often more scattered, and probably has differences for different compositions and processing (discussed later), there are marked differences between that data and data for CVI composites.

Before addressing these basic differences for different basic composite processing methods, first note similarities and differences of the CVI SiC composite data. There are several sources of strength data for the same basic CVI SiC composites, but the data from different investigators is in reasonable agreement, indicating similar trends and thus basic consistency of these results. While there is only one source of Young's modulus (E) data [2, 3], this is also a major source of strength data, allowing more definitive comparison. This shows that while both Young's modulus and strength decrease in a linear fashion on plots of the log of the property versus a linear scale for the volume fraction porosity to $P \sim 0.5$–0.6, but strength gives a higher slope, i.e., a *b* value of ~ 4.6 versus ~ 3 for Young's modulus. The higher slope (*b* value) for strength may reflect some effects of using data beyond the linear region, i.e., into the rollover region. However, somewhat higher *b* values are not uncommon for strength versus elastic moduli due to greater sensitivity of strength to more porous regions [1, 7, 8]. The other difference between the strength and the Young's modulus data is that the strength data extends to much higher P levels, with an increasing rate of strength decrease (i.e., a rollover)
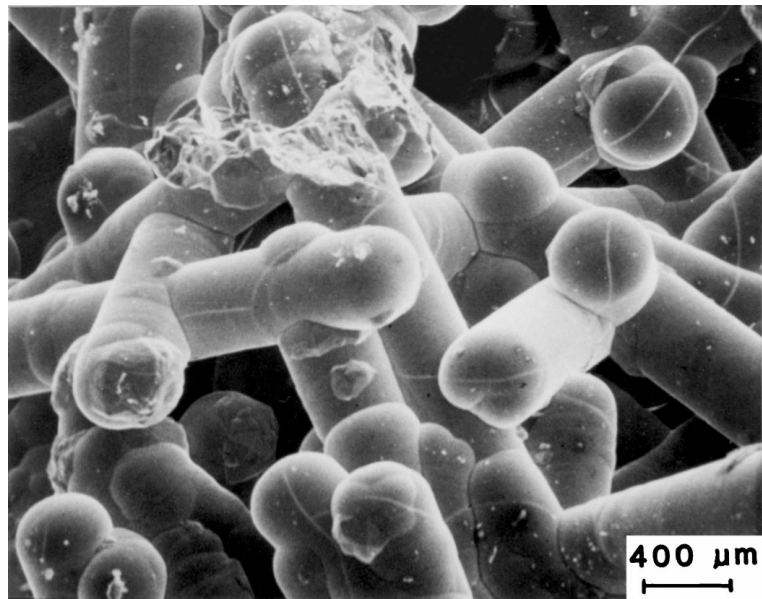
Figure 3 SEM micrograph of CVI of a fiber preform showing exclusive deposition on the fibers and rounding of sharp corners. Original photo courtesy of Drs. A. Cupto of ORNL and W. Lackey of Georgia Tech. Published with permission of Noyes Publications.

at and beyond $P \sim 0.5$–0.6. However, such increased rates of property decrease at higher porosity are typical of the porosity dependence of monolithic ceramics and other materials [1, 7, 8], being required for properties to approach zero levels at $P = P_C \leq 1$, which in this case is at $P > 0.9$ for strength. Thus, extension of the Young's data to higher porosity would continue to follow a trend similar to that for strength. Also note that both the strength and Young's modulus data extrapolate to values consistent with those of dense SiC bodies with $P = 0$ and fine grain size (e.g. CVD) bodies. Thus, the strength and Young's modulus data are consistent with each other, with strength showing somewhat faster decrease with increasing porosity as frequently occurs due to its greater sensitivity to porosity heterogeneity. Finally, note that the linear behavior to $P \geq 0.5$, the modest slopes of ~ 3 to <5 extending to $P > 0.5$ on the semilog plots of Figs 1 and 2, and the high P values where properties approach zero, i.e., $P_C < 0.9$ for the strength data, are all consistent with both modeling and data for pores of an ellipsoidal or spherical character [1, 7, 8], which is expected from and observed in CVI matrices (Fig. 3).

Next consider a key factor in this note, namely the differences between the above porosity dependence of the CVI composites and data for fiber composites where matrices are obtained by hot pressing glass or crystalline ceramic powders or by pyrolysis of preceramic polymers. The marked contrast in the P dependence of strengths between this second group of composites and the CVI composites is two fold. First and most important is the initial high rate of strength decrease with increasing P at low P for the composites processed by other methods than CVI. These rates, i.e., b values of 14–21, are 2–4 times average values for normal ceramics and most other porous materials [1, 7, 8] and 3–7 times those for the CVI composites. Second, where data for these other composites extends to higher porosity levels, their rate of strength loss with increasing P be-

comes very low, i.e., b values of <1 to <2, which are lower than found for normal porous ceramics and other materials at any P level, let alone at such substantial P levels. Thus, these other composites show opposite trend with porosity from those of CVI composites; the former showing high initial and low subsequent rates of property decreases with increasing P, while CVI composites show the opposite trends, i.e., low initial decreases followed by high rates of decrease.

A key question is thus what is the source of this pronounced difference in the porosity dependence of CVI composites versus that of composites from hot pressing or polymer pyrolysis. While there is no detailed porosity characterization available for any of these composites beyond measured P values, available data and basic pore-source and location [1, 7, 8] provide insight that has important ramifications for processing and performance of differing ceramic fiber (and possibly other) composites.

The differences between CVI and other ceramic fiber composites can be first seen by recalling that the basic nature of CVI is to deposit on existing solid surface which in the case of fiber composites is on the fibers. Thus, CVI matrices develop from the fiber outward which thus moves the pores initially existing between the fibers away from the fiber surfaces. Further, deposition tends to fill narrower areas between fibers sooner, i.e., tending to round out such areas [13] and sharp corners (Fig. 3). With substantial deposition this results in the interstices between fibers approaching spherodized or rounded tubular pores nominally in the center of the interstices between the fibers. Again these remaining pores are clearly removed from the fiber surfaces to the extent that deposition is carried out.

In contrast of CVI matrix processing, hot pressing of powders to produce matrices for fiber composites results in two general locations of (mainly finer) pores, namely between the matrix particles and between these particles and the fibers. The latter are typically more

difficult to eliminate and are likely to deviate more from the nonspherical shapes of pores between grains, i.e., toward thinner and more cusp-shaped, pores due to limited wetting and greater difficulty of fiber matrix particle bonding. Composites with matrices derived from polymer pyrolysis will have pores formed in the matrix that are spherical [1] and hence more equiaxed and more benign in decreasing properties [1, 7, 8] than pores between particle derived matrices. However, while the matrix preceramic polymer may wet the fibers, their surfaces are a very likely location for forming of pores, e.g. due to decomposition gases from the polymer precursor. Again, surface energies are likely to result in such matrix-fiber interfacial pores being rather narrow, cusp shaped, and probably elongated along the fibers. The resultant expected matrix-fiber interfacial pores from either powder or preceramic derived matrices provide an explanation for the bilinear dependence of strength on P (and expected similar E-P dependence) as follows.

Both the location of pores in CVI composites being away from the fiber-matrix interface, and especially their rounded, partly tubular or spherical shape [13] are very consistent with moderate rates of Young's modulus and strength decreases with increasing P and the resultant substantial limiting P level where properties approach zero. The marked contrast in the porosity dependence of strength of fiber composites with matrices formed by either polymer pyrolysis or hot pressing (or sintering), namely a very rapid initial rate of strength decrease with increasing P is attributed to the substantial fiber-matrix interfacial porosity. Like grain boundary porosity, such interfacial porosity, is expected to result in much more serious property decreases [1]. However the effects of such interfacial pores in fiber composites is expected to be more serious due to such pores limiting stress transfer across fiber-matrix boundaries for good composite mechanical performance.

Further, interfacial pores in matrices from consolidated powders are expected to be more difficult and slower to be eliminated in contrast to earlier, faster densification to eliminate pores in the matrix, the latter pore elimination by itself contributing only a limited amount to strength increases. On the other hand, decreasing interfacial porosity, which is expected to occur more as processing is approaching limited porosity, should increase strengths faster. Thus, the combination of these factors are probable reasons for low b values at higher P and high b values at low P. Such effects are likely to be quite variable, e.g. depending on fiber size, grain structure and size, and processing, hence a source of both variation and scatter, which is common and often substantial for such fiber composites, giving wider scatter of properties of composites with preceramic polymer or powder derived matrices.

Differences between the porosity dependencies of the non-CVI also appear consistent with expected pore character in the different composites. For example, the lower b values for both branches of the bilinear curves for the polymer pyrolysis matrix (Fig. 2) would be consistent with its porosity in the bulk of the matrix being generally spherical. This is also suggested in the SiO_2 matrix data and is not necessarily inconsistent with the glass-carbon fiber data given possible variations in the mean trends. Such mitigated trends would be consistent with more spherical character of pores within the matrices expected in both generally amorphous matrices. The most extreme decreases in mechanical properties of composites with crystalline matrices derived by sintering mechanisms is consistent with pores between packed and partially sintered particles being more serious source of property reduction.

3. Summary and conclusions
Thus, the known and expected pore character in ceramic fiber composites with matrices made by either powder consolidation or polymer pyrolysis or by CVI provides an explanation for the markedly different porosity dependencies of their mechanical properties. These differences are a very rapid initial, then a much slower decrease in properties as porosity increases for the former versus the reverse for CVI composites. This evaluation has significant implications for composites made with some residual porosity (especially by sintering) and the possibility of using porous fiber coatings to enhance resistance to oxidative embrittlement. However, much more extensive and detailed study of the porosity dependence of fiber composites is needed. Characterization of the pore structure as a function of porosity and composite matrix processing is particularly needed.

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