Ceramic Matrix and Resin Matrix Composites: A Comparison

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Abstract
The underlying theory of continuous fiber reinforcement of ceramic matrix and resin matrix composites, their fabrication, microstructure, physical and mechanical properties are contrasted. The growing use of organometallic polymers as precursors to ceramic matrices is discussed as a means of providing low temperature processing capability without the fiber degradation encountered with more conventional ceramic processing techniques. Examples of ceramic matrix composites derived from particulate-filled, high char yield polymers and silsesquioxane precursors are provided.

1. INTRODUCTION
The increasing acceptance of resin matrix composites as structural materials for aerospace applications has led to a heightened interest in extending the use of composites to higher temperatures, particularly in engine environments. Ceramics, because of their stability at elevated temperatures, offer significant potential in engine applications; however, their use has been limited by their brittle fracture behavior and high degree of flaw sensitivity. The incorporation of particulates, whiskers or continuous fibers into a ceramic matrix could provide mechanisms for "toughening" the ceramic, increasing reliability by decreasing flaw sensitivity, and, in the case of continuous fibers, ameliorating the tendency toward catastrophic failure.

The base of knowledge gained with resin matrix composites can in part, serve as a base for the development of structural ceramic composites. However, there are important differences between ceramic matrix and resin matrix composites in fabrication, microstructure, physical properties and mechanical behavior. This paper offers a comparison of the two, as well as a discussion of opportunities for the utilization of
organometallic polymers as precursors to ceramic composites. The focus will be on continuous fiber reinforced materials.

2. THEORY

In resin matrix composites typically the fiber modulus and strength are much greater than those of the matrix. The fiber, therefore, provides stiffness and load bearing capability, while the matrix serves to distribute the load among the fibers. Often, especially in the case of epoxy matrix materials, a coupling agent is introduced to enhance the strength of the interface, increasing load transfer capability from matrix to fiber. The strain capability of the matrix typically exceeds that of the fiber; hence, initiation of fracture is from the failure of a fiber or group of fibers. The load is then redistributed to the remaining fibers until additional fiber breakage occurs.

In contrast, in a ceramic matrix composite the moduli of the fiber and matrix typically are very similar. The fiber therefore is not the source of stiffness or necessarily of strength for these materials (1). Monolithic ceramics offer sufficient strength for structural applications, so incorporation of fibers is not necessary to achieve load bearing capability. Rather, the fiber is relied upon to bridge cracks or flaws in the matrix. Because of differences in processing between resin and ceramic matrices, the ceramic matrix is anticipated to have a higher population of processing introduced flaws and microcracks than its resin counterpart. The strain capability of the fiber is expected to exceed that of the matrix. Hence, matrix failure precedes fiber fracture. Microcracking of the matrix may provide some toughening as well as some pseudoplasticity (2-4). The desired mode of failure is debonding at the interface. Because ultimate matrix strain, $\varepsilon_m$, is less than ultimate fiber strain, $\varepsilon_f$, fiber fracture would result in brittle failure of the material. By bridging microcracks or flaws, the fiber can increase the strain to failure of the composite over that of the monolithic (see Figure 1), imparting non-catastrophic failure. If the fiber/matrix interface is not strong, cracks can propagate around the fibers rather than through them. Therefore, the primary role of the fibers in a ceramic matrix composite is crack bridging and toughening by matrix crack blunting and debonding at the interface, as opposed to providing stiffness and strength in the resin matrix composite.

3. FABRICATION

Resin matrix composites typically are processed at relatively low temperature (<350°C). The polymer resin may be either a thermoplastic or thermoset, but typically will undergo viscoelastic
flow, providing a means of fiber impregnation and matrix consolidation.

Glasses do become molten, and offer the advantage of forming glass matrix composites by hot pressing or transfer molding. A number of glass matrix composites have been studied (5-7). However, the melting points of many glasses are sufficiently high so that reaction with the fiber can become a problem. As with resin matrix composites, the use temperature of glass matrix composites will be well below their softening point. Carbon reinforced glass composites have been reported which offer zero coefficients of thermal expansion (7).

Ceramics, by contrast, do not melt flow at temperatures low enough for composite fabrication. Conventional sintering and hot pressing temperatures usually exceed those at which available fiber reinforcements degrade in strength.

Oxide ceramic matrices can be formed by sol-gel processing (8-9). Ceramic composites can also be fabricated by chemical vapor infiltration (CVI) or by chemical vapor deposition (CVD) (10-11). Silicon nitride matrix composites have been fabricated successfully by reaction bonding of silicon powder in a nitrogen atmosphere (12-13). Organometallic polymers also might serve as precursors which can be pyrolyzed to a ceramic char (14-24); these are discussed in greater detail below. In addition, porous carbon chars can be formed by polymerization around a pore former, and the resulting porous carbon reacted with silicon to form silicon carbide (25). All of these techniques can be expected to produce matrices with rather high levels of porosity (up to 35 - 40 percent), as opposed to perhaps <3 - 5 percent porosity typically found in resin matrix composites. How well this porosity can be tolerated will depend on the uniformity of pore size and distribution and the diameter of bridging fibers.

4. FIBERS

Resin matrix composites can be fabricated from a wide variety of fibers, offering a broad choice of modulus and strength for tailoring to particular applications. The selection of fibers available for ceramic composites is much more limited, however, due to the higher temperatures required for composite processing and in use.

Carbon fibers have been used with glass matrices to temperatures of about 600°C (7). However, at higher temperatures carbon will react to form carbides and will be extremely susceptible to oxidation when used in a porous matrix.

SiC fibers would offer good modulus and high temperature properties. Large diameter (140 μm) SiC fibers produced by CVD are available with temperature capabilities to 1400°C (26), but their diameter precludes their use in woven structures
or in the formation of complex shapes. For strengthening a ceramic matrix, interfiber spacing less than the critical flaw size is needed; this requires fiber diameters to be smaller than the interfiber spacing. The ultimate matrix tensile strain also is influenced by fiber diameter and the strength of the fiber-matrix interface (2).

Available small diameter fibers include polymer-derived Nicalon SiC and oxide fibers such as Nextel 312, 440 and 480 (27), comprised of boria, alumina and silica, and FP-alumina (28). However, all of these become thermally unstable at temperatures from 1000 to 1200°C.

5. PHYSICAL AND MECHANICAL PROPERTIES

In any composite system where there is a difference in coefficient of thermal expansion (CTE) between fiber and matrix, residual thermal stresses will be expected to develop during both composite fabrication and on thermal cycling. For most fibers, expansion is anisotropic, differing along the fiber axis and the radial direction. A pure β-SiC fiber might prove to be the exception.

When graphite fiber is used as the reinforcement, the CTE along the fiber axis is slightly negative. Residual stresses developed during fabrication place the fiber in compression and the matrix in tension. In any ceramic composite fabrication approach in which matrix shrinkage takes place, and especially in polymer derived materials, the matrix will likely be in tension as well. However, since ceramic matrix composites can be expected to see high temperatures both in fabrication and in service, the residual stresses are expected to be much greater than in their resin matrix counterparts, and may give rise to microcracking on fabrication. In terms of designing with composites this leads to a significant difference between resin and ceramic matrix materials. Whereas resin, glass and probably RBSN matrix composites can be designed as a crossply layup of unidirectional lamina, ceramic matrix composites in which matrix shrinkage occurs in processing likely will have to be fabricated from 2D cloth or as 3D woven structures to minimize shrinkage cracking.

Some ceramic matrix composites might alleviate the problem of residual stresses by choice of fibers with high axial CTE's relative to the matrix, which would place the matrix in compression. However, if the CTE of the fiber is much greater than that of the matrix, debonding of the interface will result (3).

Decreased matrix strain capability relative to the fiber may decrease tensile strength, as the matrix cannot plasticly deform to accommodate stress concentrations. Behavior under flexural loading might become more complex. Prewo
(6) has studied Nicalon/epoxy and Nicalon/lithium aluminosilicate (LAS) composites in both tension and flexure, and notes that while the Nicalon/epoxy composites had the higher tensile strength, in flexure the LAS matrix material appeared stronger as it "yielded" due to microcracking, shifting the neutral axis of the beam toward the compressive side of the test specimen. Thus, ceramic composites may appear to have greater strength in flexure than their resin matrix counterparts as a result of both their higher matrix compressive strength and the pseudopseuductility imparted by microcracking.

Microcracking also can become a problem to the environmental stability of the fibers in air, leading to fiber degradation and fracture during use at elevated temperature.

6. POLYMERIC PRECURSORS TO CERAMIC MATRICES

The use of organometallic precursors which can be pyrolyzed to a ceramic char provides a means for forming ceramic matrices utilizing the advantages of ease of fiber infiltration, control of rheology and low temperature processing typical of resin matrix composites. Choice of polymer is influenced by stoichiometry of the resulting char and shrinkage on pyrolysis. Ideally, the closer to stoichiometric SiC or Si₃N₄ the final product, the more thermally stable it may be expected to be. Also, the smaller the weight loss and volumetric shrinkage on pyrolysis, the less the need for multiple re-impregnation cycles and the less the likelihood of large cracks.

A number of organometallic polymers have been studied; some of these are shown in Table I. The polycarboxilane work of Yajima (14-16) serves as the basis for Nicalon fibers. The char is rich in excess carbon. It also contains oxygen intentionally introduced as a crosslinking agent to stabilize the fiber structure prior to pyrolysis. The deviation from stoichiometry results in thermal instability above 1200°C.

Most of the polysilanes and polycarboxilanes listed undergo weight losses of 40-60 percent on pyrolysis. Higher char yields have been demonstrated for the polysilazanes; 80-85 percent char yields have been reported by Seyferth (23). The polysilazanes are, however, moisture sensitive, and require composite processing to be carried out in inert atmospheres.

Recent work in our laboratory (29) has examined a group of silsesquioxanes (Figure 2) having the general structure RSiO₁₋₅, where R = methyl, phenyl, propyl, or vinyl, as SiC precursors. The silsesquioxanes melt flow, thermally crosslink, and then can be pyrolyzed at nominally 500°C. At higher temperatures they can be expected to undergo a carbothermal reduction to SiC with loss of CO (Figure 3). By controlling the starting ratio of
Si/C we hope to control the stoichiometry of the end product.

Microstructure of Nicalon/silsesquioxane composites is shown in Figures 4 and 5. Initial impregnation shows few voids. After pyrolysis followed by heating to 1000°C in argon, matrix shrinkage and pore formation are evident (Figure 4). The darkest phase seen in the optical micrograph (Figure 4h) is epoxy which was vacuum infiltrated into the composite after pyrolysis for polishing, and shows the extent of matrix cracking. The composite might be reimpregnated with silsesquioxane and again pyrolyzed to increase matrix density.

Matrix surface cracks both parallel and perpendicular to the fibers also are observed (Figure 5), with the more matrix rich surfaces showing the higher extent of cracking. These cracks likely arise from a combination of shrinkage on pyrolysis, mismatch in CTE between fiber and matrix and anisotropic fiber expansion.

We also have studied a SiC particulate filled, high char yield carbon resin (30) which introduced the particulate third phase as a means of minimizing matrix shrinkage and cracking. We were able to fabricate unidirectional composites with very low pore volumes and few cracks on a single impregnation and pyrolysis cycle, provided that we used small fiber tow sizes and fibers which were not uniformly cylindrical (compare Figures 6 and 7). However, strain capability of the matrix was low (~0.3%), and tensile specimens failed in shear in the tab region. Stress-strain behavior was linear to fracture. Cross-ply layups showed extensive matrix cracking and delamination, the result of residual thermal stresses.

Jamet et al. (31) have shown that additives of a BN particulate to a polyvinylsilane minimizes linear shrinkage and weight loss on pyrolysis. Thus, the concept of particulate filled precursors would seem to warrant further study.

New polymers which yield more stoichiometric ceramic products, as well as small diameter, thermally stable fibers are needed, as is a greater understanding of the pyrolysis process and resulting stresses at the fiber-matrix interface, for major advances in new ceramic composite materials to be achieved.

ACKNOWLEDGMENTS

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<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Reference</th>
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<tr>
<td>polycarbosilane</td>
<td>((-\text{Si}-\text{C}-)_{n})</td>
<td>14-16</td>
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<tr>
<td>polyvinylsilane</td>
<td>(\text{CH}_2) (\text{CH}<em>3\text{Si}(\text{Si})</em>{n}\text{Si-CH}_3) (\text{CH=CH}_2)</td>
<td>21</td>
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<tr>
<td>polyborosiloxane</td>
<td>(\phi\text{Si} \text{O} \text{B-O} \text{B-O} \text{Si} \phi) (\phi = \text{phenyl})</td>
<td>16</td>
</tr>
<tr>
<td>polysilastyrene</td>
<td>((-\text{Si}-)_{n})</td>
<td>17</td>
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\(R = \text{CH}_2\)
Figure 1 - Theoretical stress strain behavior for ceramic matrix composite fiber bridging of matrix cracks. (Figure courtesy of Dr. James A. DiCarlo).

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egin{align*}
2 \text{SiO}_{1.6} + 5 \text{C} & \rightarrow 2 \text{SiC} + 3 \text{CO}\uparrow \\
\text{SiO}_{1.6} + \text{C (excess)} & \rightarrow \text{SiC} + \text{C} + \text{CO}\uparrow \\
\text{SiO}_{1.6} + \text{C (deficient)} & \rightarrow \text{SiC} + \text{SiO}_2 \\
& \quad + \text{SiO}\uparrow + \text{CO}\uparrow
\end{align*}
\]

Figure 3 - Possible carbothermal reduction products of silsesquioxanes based on the Si/C ratio in the starting polymer.

Figure 2 - Silsesquioxanes may exhibit either an extended cross-linked (T resin) or double ladder structure, or a mixture of the two. The extended structure is more prevalent when \( R = \text{phenyl}. \)

Figure 4 - Nicalon/silsesquioxane composite (a) as fabricated and (b) after pyrolysis followed by heating to 1000°C in argon.
Figure 5 - Surface cracking of Nicalon/silsesquioxane composite (a) on pyrolysis at 525°C for 2 hours and (b) after heating to 1000°C in argon.

Figure 6 - Celion reinforced high char yield poly(arylacetylene) matrix filled with SiC particulate showing (a) layering of fiber rich and matrix rich regions and (b) matrix areas devoid of particulate (arrows).

Figure 7 - (a) Nextel and (b) Nicalon reinforced SiC particulate filled poly(arylacetylene) matrix. Composite homogeneity is enhanced when fibers cannot close-pack (Compare Figure 6).
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