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Approaches to Polymer-Derived CMC Matrices

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APPROACHES TO POLYMER-DERIVED CMC MATRICES

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SUMMARY

The use of polymeric precursors to ceramics permits the fabrication of large, complex-shaped ceramic matrix composites (CMCs) at temperatures which do not degrade the fiber. Processing equipment and techniques readily available in the resin matrix composite industry can be adapted for CMC fabrication using this approach. Criteria which influence the choice of candidate precursor polymers, the use of fillers and the role of fiber architecture and ply layup are discussed. Three polymer systems, polycarbosilanes, polysilazanes, and polysilsesquioxanes, are compared as candidate ceramic matrix precursors.

INTRODUCTION

A growing variety of polymers which can be converted to ceramics by pyrolysis have been proposed. Polycarbosilanes and polysilazanes are among the better known families of organosilicon polymers which have been investigated as precursors to fibers and matrices for ceramic composites. Polycarbosilanes, which are converted to Si-C (and often Si-C-O), serve as the basis for Nicalon fiber (refs. 1 and 2). The oxygen incorporation can be deliberate, as is the case in Nicalon processing, where oxygen serves as a crosslinking agent (ref. 3), or by incorporation of oxygen from moisture, most often subsequent to synthesis. In some instances, including polymerization of the Nicalon precursor, the polycarbosilane is formed from moisture-sensitive polysilanes, by insertion of a methylene group into the polymer backbone (ref. 4). Such oxygen incorporation into the polymer gives rise to formation of an amorphous silicon oxycarbide phase in the fiber. Loss of SiO and CO is observed on heating the fiber above 1200 °C (ref. 5), followed by crystallization of SiC and a loss of fiber strength (ref. 6).

A large variety of polysilazanes (refs. 7 to 14) which form Si-N and Si-N-C materials, depending upon the initial polymer backbone structure and pyrolysis environment, have been reported (refs. 9 and 15). Again, oxygen may be presented in the final ceramic, although the silazanes are less moisture sensitive than the polysilanes. (Oxygen incorporation typically is <4 percent, and can be <1 percent with careful handling.)

There also has been a growing interest in the development of silicon oxycarbides from polymers of alkoxysilanes (refs. 16 to 21). These oxycarbides have been shown to form materials stable to high temperatures (1400 to 1500 °C). Also, of more recent notice, are polymers incorporating Si-N-B (refs. 22 and 23) and Si-C-Ti (refs. 24 to 27) which remain amorphous to temperatures as high as 1800 °C (ref. 23), or can crystallize to mixed phase systems.

This paper focuses on a discussion of three polymeric systems under investigation at NASA Lewis Research Center: polycarbosilanes, polysilazanes, and polysilsesquioxanes, and centers on the current status of these polymers as candidates for matrix precursors in the fabrication of ceramic matrix composites (CMC).

CRITERIA FOR COMPOSITE FABRICATION

The utilization of polymers as matrix precursors offers the advantages of low temperature processing to avoid possible fiber degradation which can occur at the temperatures required by traditional ceramic processing; the ability to form complex shapes without need for machining of ceramics; and the capability of being able to use techniques and equipment well known to the resin matrix composite industry for the fabrication of two-dimensional laminate composites and infiltration of three-dimensional preforms. To take advantage of traditional resin matrix composite processing places two important requirements on the polymer: (1) appropriate rheology to achieve flow at low processing temperatures during the first processing cycle, and to allow for reinfiltration of the pyrolyzed composite through a number of impregnation and pyrolysis cycles and (2) some secondary crosslinking mechanism (thermosetting characteristic) to aid in matrix consolidation. The first requirement necessitates that the polymer either be a liquid or melt flow. Typically, the organometallic "polymers" synthesized are better described as oligomers, as they do not exceed a few thousand in molecular weight (M_n < 1000 and M_w of <2000 is typical), and are low viscosity liquids. This is a plus for infiltration, but can present problems during composite fabrication unless mechanisms are built into the polymer structure which increase branching and crosslinking during staging and subsequent matrix consolidation.

Much of the early work on preceramic polymers placed an emphasis on achieving a ratio of elements in the polymer close to that desired in the final ceramic product. Subsequent studies have shown that polymer structure and crosslinking are of overriding consideration in attaining the desired ceramic composition. It is known, for example, that increasing chain length in alkyl substituents to Si does not increase C content in the final ceramic, as these alkyl groups are cleaved during pyrolysis; however, alkenyl or aryl substituents do influence char composition (ref. 28). Branching and crosslinking also greatly increase char yields (ref. 29), thus minimizing shrinkage and accompanying matrix cracking. Pyrolysis times, temperatures and environmental conditions also determine char yields and ceramic composition. Nitrogen can be incorporated into polycarbosilanes, and carbon removed from polycarbosilazanes, through choice of pyrolysis environments (ref. 15).

Consideration also should be given to the issue of crystalline versus amorphous ceramic matrices. Initially, following polymer pyrolysis, an amorphous ceramic matrix is formed. Subsequent thermal treatments for longer times and/or to higher temperatures can lead to crystallization, accompanied by a large volume change. The time/temperature conditions for crystallization depend on the initial polymer and polymer structure, pyrolysis conditions, intrinsic thermodynamic instabilities at higher temperatures which give rise to evolution of volatiles and progression toward stoichiometric ceramic compositions, and distribution of elements such as C in Si-C-O systems and B in Si-N-B systems, which would inhibit crystallization. Though a stoichiometric ceramic ultimately should be the most thermodynamically stable, a system which can remain amorphous to extremely high temperatures could be very desirable, because it typically would minimize volumetric shrinkage and associated matrix cracking.

Choice of architecture for reinforcement requires a consideration of two important factors: fiber/matrix thermal expansion mismatch, and the shrinkages which accompany pyrolysis. Fiber architecture must be optimized, (1) to minimize residual stresses, which are far greater in magnitude than those in resin matrix composites due to the much greater temperature range seen during processing and (2) to maintain the most uniform tow spacings. As the fibers will impede uniform shrinkage, the matrix can be expected to microcrack during the first pyrolysis cycle. Therefore, crossply layup of unidirectional tapes has not proven successful with many polymeric precursors, as it produces composites with a high tendency to delaminate.

The use of two-dimensional woven plies leads to an improvement in interlaminar strength. The weave architecture is important in averting large matrix cracks; experience has shown that satin weaves produce more uniform cracking than do plain weaves, and the large cracks seen between crossover points in the plain weaves are averted.

Of critical importance is an understanding that any woven architecture will lead to two types of fiber spacings: those within a tow, which are relatively small, and those between tows, which are considerably larger. Developing techniques for dealing with this bimodal distribution of "pore" channels which need to be infiltrated is important both to the polymeric precursor approach to matrix fabrications and to other approaches, including chemical vapor infiltration (CVI) and particulate or slurry infiltration.

Fillers can be used during the initial fabrication cycle to partially fill large pores between plies as well as between tows, leading to a more uniform distribution of remaining pores and minimizing matrix shrinkage and cracking (ref. 30). Such fillers can be produced by pyrolysis or partial pyrolysis and subsequent milling of the same polymer which will serve as a binder or infiltrant, or can be other small particle size ceramic powders.

Stacking orientation of two-dimensional plies influences the "pore" spacings between adjacent plies, as well as the residual thermal stresses present in the composite which contribute to matrix cracking. Reversing every other layer in a two-dimensional cloth is important in minimizing residual stresses which arise from weave geometry (ref. 31). In three-dimensional composites, architecture must be very carefully designed as not to produce spaces which are so large that they are never adequately infiltrated, or introduce mechanically weak matrix rich regions.

POLYCARBOSILANES

The polycarbosilanes which are precursors to Nicalon fiber are synthesized as polysilanes (-Si-Si-backbone) with substituent methyl groups, which can be converted to polycarbosilanes (-Si-C- backbone) by insertion of the methyl group into the polymer backbone on heating (ref. 4). We have synthesized polycarbosilanes directly by polymerization of alkenylsilanes utililizing a transition metal catalyst (refs. 32 and 33). We also have established that polymerization of alkylsilanes, using this same catalyst, produces polysilanes exclusively, but that copolymerization of alkyl- and alkenylsilanes can be used to produce copolymers having mixed (-Si-Si-), (Si-C-) and (Si-C-C-) backbone structures. Copolymer composition can be used to control the ratio of C/Si in the ceramics attained upon pyrolysis, and polymers have been synthesized which convert to stoichiometric SiC.

These polymers all are low molecular weight liquids which, on their own, do not consolidate well during composite lamination. However, incorporation of a difunctional silylalkane, 1,2-disilylethane (BSE) (ref. 33) provides a crosslinking site when added in small amounts to vinylsilane polymers. These polymers can be coated onto two-dimensional satin weave cloth from dry solvents under inert conditions, staged to an appropriate level, stacked in a mold and hot pressed using conditions common in the fabrication of resin matrix composites. Following hot pressing, the green composites are stable when removed from the inert environment which has been maintained up to this point. The panels can then be pyrolyzed free standing in an inert environment and reimpregnated and pyrolyzed through several iterative cycles to further matrix densification. At this point in time the fabrication of composites having a Nicalon eight harness satin reinforcement is undergoing optimization.

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POLYSILAZANES

A large variety of polysilazanes have been reported in the literature (refs. 7 to 14). On pyrolysis, a group of amorphous ceramics can be produced in which the ratios of Si, N, and C vary widely depending on the structure of the starting polymer, the degree of branching or crosslinking, and the pyrolysis conditions. The elemental composition of the resulting ceramic would be expected to influence the occurrence of crystallization, thermodynamic stability, and such physical properties as expansion coefficient, modulus, and thermal conductivity. At this stage it is unclear what ratios of Si, C, and N would be most desirable. Our fabrication efforts in this area are relatively new. As a starting point, we currently are developing fabrication techniques using commercially available polymers. Unfortunately, the number of commercial sources for these materials has been declining.

The polymer we have selected for initial study contains vinyl substituents which serve as crosslinking sites during composite fabrication. On pyrolysis in inert environment the ceramic composition attained is 42% Si, 28% N, 28% C, and <1.5% H and O by weight. Composite fabrication using inert conditions follows procedures used with the polycarbosilanes.

POLYSILSESQUIOXANES

Alkylmethoxy- or alkylethoxysilanes can form polysilsesquioxanes having the general structure $(RSiO_{1.5})_n$, (ref. 34). Depending upon polymerization conditions and the nature of the alkyl group, these polymers can form gels, or can be maintained as linear or branched polymers. Control of the linear polymer structure produces liquid polymers whose rheology can be tailored and which are suitable for composite fabrication and as infiltrants. On pyrolysis the polysilsesquioxanes convert to amorphous silicon oxycarbides (ref. 21). This silicon oxycarbide structure is maintained to 1200 to 1300 °C. On further heating to 1400 °C the oxycarbide structure is lost, leaving primarily amorphous Si-C and amorphous silica. Nanocrystallites of SiC also may be present, depending on the starting polymer composition and pyrolysis conditions. Above 1500 °C carbothermal reduction takes place, accompanied by rapid mass loss.

Copolymerization of alkylmethoxysilanes allows control of the carbon content of the pyrolyzed material. The amount of carbon which can be incorporated into the oxycarbide network is, however, limited, and any remaining carbon is present as amorphous carbon at lower temperatures (1000 °C), or graphitic carbon at higher temperatures (1400 °C). The carbon is very finely dispersed in the oxycarbide matrix, and oxidizes very slowly. The actual upper use temperature of these oxycarbides in an oxidizing environment remains undefined, but may depend upon the structure of the particular oxycarbide and the quantity and distribution of the free carbon.

Recent work (refs. 34 and 35) has shown that if Si-H bonds are incorporated into the initial polymer structure the formation of free carbon can be minimized, and presumably the stability of the pyrolyzed material in oxygen increased.

The polysilsesquioxane precursors are of interest in themselves as composite matrices; composites having tensile strengths on the order of 225 MPa and strain to failure of nominally 0.4 percent have been produced (ref. 36). Control of carbon content could be expected to influence the thermal expansion, modulus, and perhaps thermal conductivity of the oxycarbide material. This polymer system also has proved extremely useful in developing composite fabrication techniques, as they can be processed in air.

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CONCLUSIONS

Since the work on polycarbosilanes as preceramic polymers published by Yajima in the mid 70's, the interest in synthesizing new polymeric precursors has continued to grow, and has seen a rapid proliferation over the past several years. The discussion of the utilization of these polymers as matrix materials, however, remains more limited, partially as a result of the difficulties encountered in synthesizing many of them on any scale, and the lack of a market to drive scaleup.

Successful composite fabrication requires that rheology of the preceramic polymer, pyrolytic conversion, fiber architecture, and ply layup all be well controlled. Fillers can be used successfully to minimize pore size distribution, and matrix shrinking and microcracking.

Polymeric precursors to CMC matrices are attractive because of their amenability to complex shape fabrication, and their potential for fabrication of thick composites which are difficult to achieve by CVI techniques.

Of the polymer systems discussed here, the polycarbosilanes provide a unique route to C rich Si-C matrices. Polysilazanes have the greatest likelihood of producing ceramics with <1.0 percent oxygen. The polysilsesquioxanes are the easiest and most inexpensive to synthesize, and therefore the easiest to use in the development of composite fabrication techniques, as they can be handled in air, and may provide oxycarbide matrices of interest in themselves.

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