Polysilazane Precursors to Advanced Ceramics

Polysilazanes offer a convenient route to the preparation of fibers, coatings and 3-D continuous-fiber-reinforced ceramic-matrix composites that often cannot be prepared using traditional ceramic-processing methods

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Polysilazanes are polymers that consist of silicon, nitrogen, hydrogen and, in certain cases, carbon. Such polymers can be considered either "inorganic" (perhydropolysilazanes) or "organic" (organopolysilazanes or polycarbosilazanes) in nature. However, all polysilazanes contain silicon and nitrogen atoms in their backbone. Although inorganic polysilazanes contain no carbon, organopolysilazanes typically have carbon-containing groups, such as methyl or vinyl appended to silicon or nitrogen atoms within the polymer chain.

Principally because of their high pyrolytic mass yields of silicon-based ceramic material (often >80 wt%), polysilazanes have been extensively used as precursors to SiO_2,[1] Si_3N_4 and SiC ceramics.[2–8] They offer a convenient route for preparing silicon-based ceramic materials, such as fibers, coatings or 3-D continuous-fiber-reinforced ceramic-matrix composites (CMCs), which often cannot be made through traditional ceramic-processing methods.[3]

However, the use of polysilazanes in many markets has been hindered by lack of availability and price. These impediments to large-scale use derive mainly from lack of a suitable manufacturing technique. Traditionally, polysilazanes have been prepared using an ammonolysis reaction of various dichlorosilanes and trichlorosilanes in organic solvent using gaseous ammonia. The resulting NH_4CL byproduct always has been difficult to separate from the polysilazane product. Once the salt has been removed, the polysilazane has to be isolated by solvent stripping.

It is only recently that large volumes of reasonably priced polysilazanes have become available. KiON Corp. uses a liquid-ammonia process and is now able to supply multi-55-gallon drum quantities of a variety of silazane polymers to interested customers. As a result, the commercial use of polysilazanes has now expanded considerably over what it was several years ago and into many surprising markets. A variety of these applications are described herein

Inorganic and Organic Polysilazanes

Inorganic polysilazanes are currently used extensively in the electronics industry as precursors in the manufacture of dense or porous surface coatings of pure SiO_2. Such coatings can be deposited from relatively dilute solutions of perhydropolysilazanes in organic solvent (20 wt%). Conversion to SiO_2 is achieved by either allowing the deposited polysilazane coating to slowly crosslink in moist air at ambient temperature or by heating it in a water-vapor-containing atmosphere at temperatures ≤250°C. Alternatively, radiation curing (e.g., ultraviolet) can be used.

When such techniques are used, pure SiO_2 coatings that have dry film thicknesses of 50 nm to 5 µm can be obtained. Various applications for such polysilazane-derived SiO_2 coatings include thin, flexible, gas-barrier films; anticorrosion coatings for aluminum metal; and antitarnish coatings for silver and photocatalytic coatings that contain embedded anatase TiO_2 for the protection of ultraviolet-sensitive substrates. Studies have shown, for instance, that the deposition of 500 nm thick polysilazane-derived SiO_2 films on the surface of PET films decreases oxygen transmission rates through these films from 45–50 $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$ at 0% relative humidity to values that approach 0.2 $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$.

Such films also provide corrosion protection to bright, reflective aluminum surfaces at coating thicknesses of 9–10 µm, which pass aggressive, copper-accelerated salt-spray testing at exposure times >240 h (internal data, Clariant Corp.). In the manufacture of semiconductor devices, such SiO_2 coatings are routinely produced on the surface of silicon wafers by coating the silicon surface with a polysilazane-containing coating solution and then converting the coating layer of polysilazane into a SiO_2-based coating film.[9] Typically, such surfaces are prepared by spin-coating and then substantially converting the polysilazane layer to a silicon-oxide-containing ceramic, such as SiO_2. The coatings are referred to by the generic term spin-on-glass (SOG).

Recently, a body of work has focused on the ability of various organic polysilazanes to form amorphous, nonglassy silicon carbonitride (SiCN) ceramics. These ceramics are resistant to chemical degradation,[10] creep,[11–13] oxidation,[14] thermal shock, decomposition and softening.[15] Thus, they are attractive for a variety of structural ceramic and electronic applications.[16]

Electronic Ceramics

In the electronics industry, a viable new technique to fabricate ceramic devices for microelectromechanical systems (MEMS) by microcasting ultraviolet-curable organopolysilazanes has been developed recently.[17–21] This technique has been successfully used, for example, in the fabrication of a SiCN microactuator.[21] The utility of SiCN ceramics in this area derives broadly from the need for MEMS devices that can operate at temperatures >1000°C. The microactuator development effort targeted the creation of a microactuator that can operate in such extreme thermal environments and can be used to measure Young's modulus of the material from which it is constructed.

A microfabrication technique for constructing 3-D photonic crystals by deep X-ray lithography using organopolysilazanes also has been demonstrated.[22] In this process, X-ray lithography is used to make a mold that is filled with a curable liquid polysilazane that can be transformed into SiCN ceramic using pyrolysis. The technique yields 3-D photonic crystals with a lattice constant of 85 µm and rod diameter of 22 µm. The transmission spectrum shows a 3-D photonic bandgap centered at 125 µm (2.4 THz). This result is in good agreement with theoretical calculations.

A polysilazane-derived SiCN composite that has magnetic properties also has been prepared using a technique whereby Fe_3O_4 powder is batched with polysilazane and pyrolyzed. At pyrolysis temperatures of 700–1000°C, reduction of the Fe_3O_4 phase to α-Fe is observed via the reducing action of CH_4 and H_2 that are present in the pyrolysis off-gas of the polysilazane. Magnetization curves for the composite indicate that α-Fe is the predominant magnetic phase. Such composites are envisioned for use as high-temperature stable materials for use in harsh-environment applications.

Structural Ceramics

In the structural ceramics industry, monolithic and composite ceramic structures have been fabricated using organopolysilazane ceramic precursors. Two methods have been developed to prepare crack-free monolithic ceramics from polysilazanes. The first method involves a warm-pressing technique, in which the polymer is first crosslinked to an infusible state, compacted by cold isostatic pressing or warm-pressing and then pyrolyzed at a slow heating rate.[23,24] The second method involves prepyrolysis of the polymer to a ceramic powder. The powder is subsequently compounded with additional polysilazane, and the composition is cured during a pressing step.[25–27] The first method results in ceramics that have a high fraction of open porosity, whereas the second method results in much less gas generation and volume shrinkage in the resulting ceramic.

Porous monolithic ceramic bodies also can be fabricated using organopolysilazanes. Representative of this work is the preparation of high-surface-area catalyst supports made of macroporous SiCN produced using a capillary micromolding technique.[28] When this method is used, SiCN and SiC ceramic monoliths that consist of highly interconnected inverted beaded networks of uniform pores with diameters of 50 nm to 10 μm are obtained. These crack-free, porous monoliths demonstrate important material characteristics for use as catalyst supports for hydrocarbon reforming: high surface area per unit volume; compatibility with temperatures >800°C; and low pressure drop while maintaining a high surface area by having an inverted beaded bed structure to form the network of interconnected pores with a porosity >70%.

Organopolysilazanes also are useful for producing either fibers or matrices in the fabrication of CMCs. Fibers, for example, can be produced by the melt-spinning and pyrolysis of pure polysilazanes[29–31] or through the modification of polysilazanes with, for example, metal alkoxides (such as titanium or zirconium alkoxides) followed by spinning and a subsequent pyrolysis step.[32,33] In the former case, SiCN fibers are produced, whereas, in the latter case, various oxycarbonitride compositions are obtained. SiCN–ZrO_2 fibers can be prepared, for example, from liquid polysilazane precursors by reacting a vinyl-substituted polysilazane with a solution of 70 vol% tetrapropyl zirconate in isopropoanol.[33]

It is proposed that such chemical modification makes the polymer amenable to fiber drawing by producing linear chains in the polysilazane, which results in such suitable rheological behavior. Although such work has been reported using zirconium alkoxide, the idea of modifying SiCN polysilazane precursors with other metal alkoxides also has been proposed. Titanium, hafnium, silicon and aluminum alkoxides are proposed as alternatives to zirconium alkoxides in such a process.

Highly corrosion-resistant monolithic ceramics also have been prepared recently using the technique of metal alkoxide modification by the reaction of organopolysilazanes with aluminum isopropoxide.[34,35] Although fibers have not been drawn from such compositions, it has been demonstrated that polysilazane-derived SiAlCN ceramics possess much better oxidation resistance than simple SiCN ceramics. Oxidation rates an order of magnitude lower than those for pure SiCN have been measured. It also has been subsequently shown that such SiAlCN ceramics exhibit excellent water-vapor corrosion resistance at 1100°C.[35]

CMC matrices also can be generated from polysilazanes. Variations of the polymer infiltration pyrolysis (PIP) technique have been demonstrated.[36–38] PIP and resin-transfer-molding (RTM) techniques into fibrous preforms with suitable organopolysilazane precursors (e.g., low viscosity, solvent-free), followed by thermally induced crosslinking and pyrolysis at temperatures of ≥1300°C or higher, have been used. These techniques result in dense CMC materials when an iterative process of reinfiltration and pyrolysis is followed.

Using such techniques, Nicalon® and Hi-Nicalon® fiber-reinforced composites were fabricated using a liquid, vinyl-appended polysilazane precursor.[37] Nicalon® fiber-reinforced plates fabricated by infusion of C/SiC preforms and densified seven times at 1300, 1400, 1500 and 1600°C demonstrated flexural strengths of 263–447 MPa, fracture toughness of 24–30 MPa•$m^{1/2}$ and composite densities of 2.57–2.87 g/cm^3. The maximum room-temperature four-point flexural strength, 575 MPa, was demonstrated when the composite was pyrolyzed at 1300°C. The strength of the composites decreased with increased pyrolysis temperature, presumably because of the degradation of the Hi-Nicalon fibers at temperatures >1300°C.

Continuous C-fiber/SiC composites also have been produced using a low-cost manufacturing method. The porosity in a 2-D carbon-fiber preform is filled with a SiC powder using a pressure-infiltration method to produce a high-particle-packing density in the fiber preform.[39] The preform then is heat-treated at 400°C to form a porous framework that than is infiltrated with a liquid polysilazane precursor. Subsequently, the infiltrated polysilazane is pyrolyzed in argon at 1300°C. The developed C-fiber/SiC/SiCN composites are considered as promising candidates for low- and high-temperature applications, such as brake disks, seals, components of chemical reactors and gas turbines.

CMCs also have been prepared using a directed-metal oxidation process into a preform fabricated by a low-pressure pressing technique using a polysilazane binder.[40] In this process, a SiC powder preform is prepared using a liquid poly(urea)silazane binder to shape-stabilize the preform for processing at high temperatures. The ceramic matrix then is introduced into the SiC powder preform through a ceramic matrix "growth" process. The process involves the infiltration and simultaneous oxidation of molten aluminum metal into the porosity of the SiC powder preform in an air atmosphere at 900°C. Such a process has been used to produce a SiC-powder/Al_2O_3 CMC valve seat.

Organopolysilazanes also are used in the production of metal-matrix composites (MMCs), where they can serve as extreme high-temperature binders for preforms into which molten silicon or aluminum metals are introduced.[40,41] The fabrication of Al_2O_3-particulate-reinforced aluminum-metal-matrix composite brake rotors and disks with maximum operating temperatures of 482°C (900°F) using polysilazane preform binders has been demonstrated.[40] The manufacturing technique for such Al_2O_3/Al MMCs uses pressed Al_2O_3 particulate preforms, which include 2.83 wt% polysilazane binder. The aluminum-metal matrix is introduced using a pressureless metal infiltration process in a nitrogen atmosphere.

Ceramic Coatings and Joining

Organopolysilazanes also have found utility in the joining of ceramics and as the continuous phase in formulated, high-temperature coatings. Coatings and joints from filled organopolysilazanes have been demonstrated for Si_3N_4-matrix composites,[42] microwave joining of SiC,[43] seals for solid oxide fuel cells[44] and as electronic adhesives for bonding integrated circuit chips to carriers or circuit boards.[45] In this last application, a layer of a paste prepared from methylhydridopolysilazane, Al_2O_3, microballoons and glycidoxypropyltrimethoxysilane is applied between an electronic component and the substrate to which it is to be adhered. The component can be a silicon-based device, gallium arsenide-based device, focal play array, optoelectronic device, photovoltaic cell or optical device.

The assemblage then is heated to 400°C for 4 h to convert the polysilazane to a ceramic. Strong joins are obtained. Polysilazanes also have been used for preform joining in the fabrication of CMCs and MMCs.[40]

Several coatings companies are currently selling formulated ceramic coatings based on organopolysilazanes for under-the-hood automotive and truck applications (e.g., exhaust systems and pistons). Organopolysilazane-based coatings for firearms and high-temperature applications requiring substantial heat insulating characteristics also are being developed. Organopolysilazanes also have been used effectively as antioxidation layers on carbon structures,[46] C/SiC composites,[47] carbon fiber or SiC fiber[41] and in the strength enhancement of carbon foams.[48]

Graphite plates were coated with a polysilazane and then pyrolyzed in air to 1000°C. An adherent, SiO_2-containing coating was obtained.[46] When the coated sample was further heated to ≥1400°C, a β-SiC coating was obtained. When subjected to five coating and heat-treatment cycles, a 9.4 µm thick ceramic coating resulted. A ratio of weight loss of only 1.3% was realized in an oxidation test in which the coated carbon sample was heated for 20 h at 800° C.

Nanoscale Applications

Recent investigations also have shown that selective pyrolysis of organopolysilazanes under controlled atmospheres or in the presence of various organic polymers can result in ceramics with well-defined nanoscale structural features, including such novel structures as Si_3N_4 nanobelts.[49]

Controlled pyrolysis of organopolysilazanes also has resulted in the generation of ceramic nanocomposite structures with 30 nm grains.[50] The major crystalline phases are nanocrystalline SiC, Si_3N_4, a small amount of Si_2N_2O and free carbon. Heterogeneous and homogeneous crystallization is observed. The grain boundaries are free of oxide–nitride glassy phases, which indicate the possibility of high creep resistance for these nanocomposites.

Mesoporous ceramic materials also have been produced based on the use of an organic diblock copolymer structuring agent in combination with an organopolysilazane.[51] The diblock copolymer is an amphiphilic poly(isopreneblock–ethylene oxide) and is used as a method of directing structure in a polysilazane during pyrolysis. The mesoporous ceramic prepared using this technique is stable to 1500°C, and it has a lamellar nanostructure that consists of hexagonally packed cylinders with an average pore diameter of ~13 nm. ■

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