

POLYSILAZANES – A USER'S MANUAL

While, in the past, a great deal of detailed work has been done to generate coatings, ceramic monoliths, ceramic fibers, and ceramic matrix composites from organopolysilazanes, a succinct, yet comprehensive distillation of the various, generic steps involved in the handling, cure, and pyrolytic conversion of polysilazanes to ceramic materials has not been assembled. This paper will attempt to describe some of the more commonly used techniques to effect the conversion of one commercially available organopolysilazane, Durazane 1800, a low viscosity liquid, to a variety of silicon-containing ceramics.

PART 1: Various Methods That Can Be Used to Cure (Solidify) Durazane 1800, KiON HTT1800, or Ceraset Polysilazanes.

Silicon-containing ceramic precursor polymers such as polysilanes, polycarbosilanes, and polysilazanes have traditionally been used to fabricate ceramic articles such as ceramic monoliths, fibers, and composites comprising silicon ceramic material such as silicon carbide or silicon nitride. Their utility in this application resides in the ability to process these materials as polymers, and then convert the resulting configuration to a ceramic article. This contrasts markedly with traditional methods of ceramic forming that typically involve slurry casting of ceramic powder slips or pressure-forming of ceramic powders that are batched with organic binders.

By far the most commonly used polysilazane for pre-ceramic applications is the vinyl-appended Durazane 1800. This polymer has ~20% vinyl content and has a viscosity of around 25cps. The fact that this polysilazane is of such low viscosity makes it quite amenable to a variety of forming techniques, but because it is a liquid of such low viscosity, shape-stabilization must be accomplished through solidification before conversion to ceramic can be attempted. The presence of the vinyl groups in Durazane 1800 offers the option to effect liquid-to-solid conversion through several techniques, including hydrosilylation, radical polymerization, thermal polymerization and even in some instances UV light curing. Typically, these cure options require moderately elevated temperatures, however room-temperature curing options, not commonly known to the industry, are also presented here.

Simple Thermal Crosslinking

Vinyl groups are thermally labile and can be made to polymerize with nothing more than applied heat. With ~20% vinyl groups, Durazane HTT 1800 can crosslink by simply elevating the temperature to 180-200°C and holding for several hours, depending on the environment and cross section of the part being cured. While this is the simplest curing mechanism, it is also the least amenable to ceramic processing. Typical cross sections of CMC's or other ceramic applications are on the order of centimeters not millimeters. Thinner cross sections, such as those seen in thin film coatings are, however, conducive to simple thermal crosslinking since the gaseous byproducts that are evolved on pyrolysis are allowed to escape without disrupting coating integrity. However, larger 3-dimensional pieces to be processed can suffer from 'bubbles' and resulting porosity caused by gaseous species having no escape route. These

gaseous species can be low molecular weight segments of organopolysilazane, or other gasses such as ammonia, methane, or hydrogen that become trapped during pyrolysis. Thus, while it is simple and useful in certain applications, it is not recommended for 3-dimensional ceramic applications.

Hydrosilylation Crosslinking

Vinyl substituents are also susceptible to hydrosilylation reactions with silicon-hydrogen bonds, both of which are present in Durazane 1800. The typical reaction conditions include the addition of a metal catalyst, usually platinum, palladium or cobalt, to initiate the hydrosilylation. In silicone chemistry, Karstedt's catalyst is the most common and inexpensive option. However, in polysilazane chemistry, cobalt derivatives are preferred and, quite frankly, much more active. Hydrosilylation will proceed at relatively low temperatures (RT-200°C) with the addition of 0.5-2% by weight catalyst. Without any gaseous byproducts, and with a purely addition cure mechanism, hydrosilylation is a good choice for large, 3-dimensional ceramic processing.

Free-Radical Polymerization

Unsaturation organic groups, such as vinyl or allyl groups, can also undergo free-radical polymerizations using organic peroxides as initiators. When coupled with metal catalysts these reactions can be accelerated and optimized for different applications. Typical peroxide classes include dialkyl peroxides, peroxy ketals, diperoxyesters, alkyl peroxyesters, and peroxy carbonates. Acyl peroxides such as benzoyl peroxide are not recommended. Hydroperoxides are also extremely reactive, exothermic, and somewhat dangerous. The use of hydroperoxide is, thus, not recommended. Dicumyl peroxide, which is slightly soluble in the polymer without added solvent, gives an easy and effective way to cure Durazane 1800 at slightly elevated temperatures (100°C to 150°C) when added at a 0.5-1 wt% level. When coupled with metal catalysts (as those used for hydrosilylation), these cure rates can be increased and/or the cure temperature decreased.

Room-Temperature Cure

Of the several mechanisms listed above for crosslinking polysilazane polymers for use in ceramic applications, the most efficient and highest ceramic yielding method is a so-called 'room-temperature' cure. While several peroxides can be used for free-radical polymerization, and several metal catalysts can accelerate these cure rates, a particular combination of the two can achieve **very thorough** cure without relying on elevated temperatures. By avoiding elevated temperatures, the resultant, highly crosslinked 'green body' can be pyrolyzed in much higher ceramic yield while avoiding the porosity experienced by other cure mechanisms. A general rule for ceramic processing of polysilazanes is, the slower the cure, the higher the crosslink density, and the higher the ceramic yield. We offer the following protocol as a means to effect an

efficient, room-temperature cure of a vinyl polysilazane (Durazane®1800, HTT 1800, Ceraset, etc.).

1. Thoroughly mix the vinyl polysilazane liquid with any fillers, excipients, sintering aids, seeding material etc. until a homogenous mixture is achieved.
2. Add 0.5-2 wt % Luperox® 231 (1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane) to the liquid slurry and mix well. Suitable substitutes for peroxide initiators include the following: Luperox® 531M80 (1,1-Bis(tert-amylperoxy)cyclohexane and dicumylperoxide.
3. Add 0.05-0.25 wt % Iron Acetylacetonate (2,4-pentanedione iron (III)) and mix very well ensuring the iron is completely dissolved. Suitable substitutes for metal catalysts include the following: Cobalt (II) Naphthenate, Bis(2,4-pentanedionato)cobalt(II), Pt Catalysts e.g. Karstedt's catalyst.
4. Such catalyzed room-temperature cure slurries can be infiltrated, B-staged, laid-up, or molded with working times in the 6-12 hour range depending on temperature and filler load.
5. Complete cure is observed in ~5-7 days at 25°C or sooner at slightly elevated temperatures.
6. Once cured to this 'green body' stage, the material can then be subjected to pyrolysis to convert the part to ceramic.

PART 2: Pyrolysis of a Polysilazane to a Ceramic Material

Polysilazane exists as a low viscosity liquid polymer as it is manufactured. Once crosslinked thoroughly enough, through whichever of the mechanisms listed above etc., it is effectively 'solid' polysilazane polymer. This curing step results in what is known to the industry as a 'green body' and is generally directly preceded by pyrolysis. Pyrolysis, also termed 'ceramization', is the process of thermally converting the cured/crosslinked polysilazane, complete with any fillers, additives etc. into a solid ceramic material.

While polysilazanes, polycarbosilanes, polysilazanes, and other ceramic precursor polymers all share broad applicability in ceramic processing technology, ceramic precursors comprising silicon-nitrogen bonds in combination with nitrogen-hydrogen bonds are unique in certain ways. When heated, most ceramic precursor polymers undergo a precipitous conversion from their polymeric form to their ceramic form. Since these polymers normally comprise silicon atoms bonded to carbon atoms, the onset of this conversion occurs at temperatures around 500 °C, the temperature at which silicon-carbon bonds are broken, and typically occurs with a precipitous loss of mass.

By contrast, ceramic precursors containing silicon-nitrogen bonds in combination with nitrogen-hydrogen bonds all undergo transamination rearrangement reactions at temperatures of less than 500 °C before they convert to ceramic materials. This is typified in the thermal behavior of the broadest class of such polymers, polysilazanes. Depending on the chemical composition of such polysilazanes, these transamination reactions occur in different temperature regimes. For polysilazanes comprising no silicon-carbon bonds, i.e. the "inorganic"

polysilazanes or “perhydropolysilazanes”, transamination reactions can occur at temperatures as low as 25 °C. For such perhydropolysilazanes, transamination is promoted by the enhanced lability of the silicon-hydrogen bond due to the geminal configuration of Si-H bonds at each silicon atom. Hydrogen gas, as well as ammonia gas, is often a by-product of such transamination reactions. By contrast, polysilazanes comprising silicon-carbon bonds, i.e. the “organic” polysilazanes or “organopolysilazanes” are typically stable to such transaminations at room temperature and undergo transamination at higher temperatures. Typically, organopolysilazanes undergo rapid transamination in the 300 °C to 450 °C temperature regime.

Such behavior is readily apparent in the thermal gravimetric analysis (TGA) of an organopolysilazane. Whereas a typical polycarbosilane shows a precipitous loss of mass at 500°C in an inert atmosphere, a typical organopolysilazane will undergo three regimes of mass loss. The TGA shown in Figure 1 representative of the TGA observed during the pyrolysis of a polysilazane containing Si-H, Si-CH₃, and Si-CH=CH₂ groups such as Durazane 1800 (KION HTT1800).

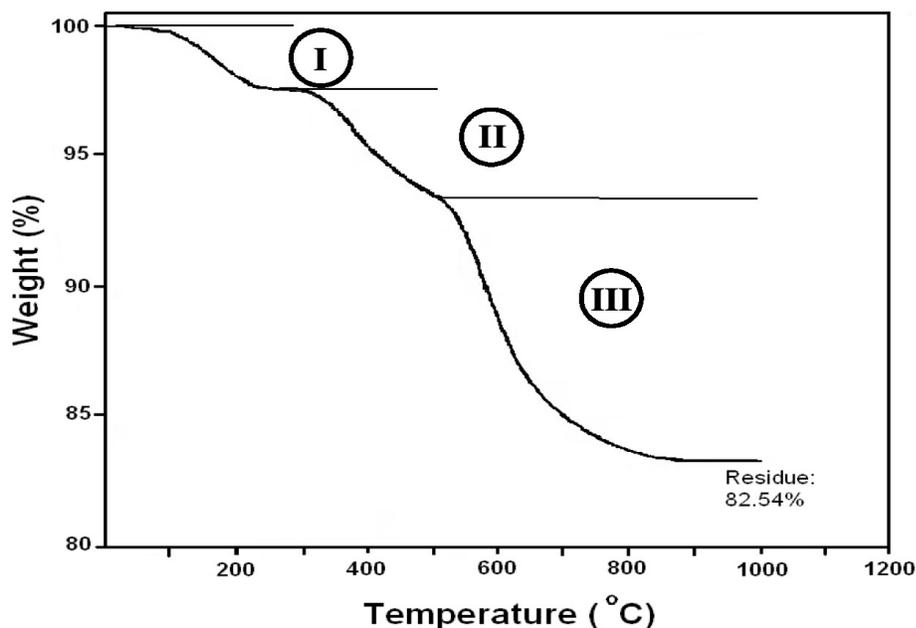
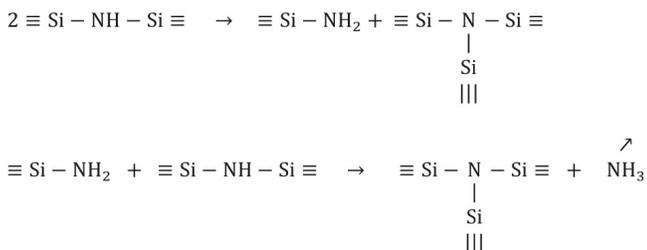


Figure 1

In Region I if the TGA (R.T. To about 250°C) low molecular weight, silicon-containing oligomers are lost. The mass loss is about 3% based on the initial weight of the polysilazane. [If the polysilazane has been first converted from a liquid to a solid state through a heat initiated cure in that temperature window, the TGA of the fully solidified polysilazane might not show such a significant degree of mass loss in this temperature regime.]

In Region II (300°C to about 450°C) redistribution of Si-N bonds through transamination reactions occurs, and mass loss occurs through the evolution of ammonia gas. The mass loss in this region is about 4% based on the initial weight of the polysilazane.

Transamination:



In Region III (500°C to about 750°C) ceramization occurs with the breaking of silicon-carbon and silicon-hydrogen bonds. This results in mass loss of material which is largely methane and hydrogen, along with some other very low molecular weight hydrocarbons. The mass loss in this region is significant and can amount to up to about 9% based on the initial weight of the polysilazane.

Beyond about 750°C very little mass loss is observed, and what little is observed consists mainly of hydrogen gas. Pyrolysis to slightly above 1,000°C is typically required to scrub all of the hydrogen from a pyrolyzed polysilazane.

Another way to view this is to overlay the evolved gaseous species onto the temperature scale above as shown in Figure 2. When this is done the thermal regimes in which each of these species is evolved becomes evident:

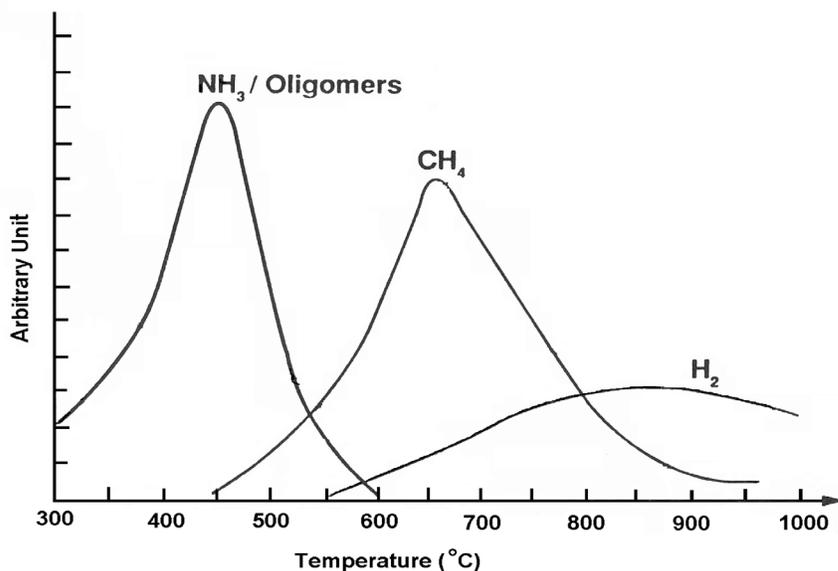
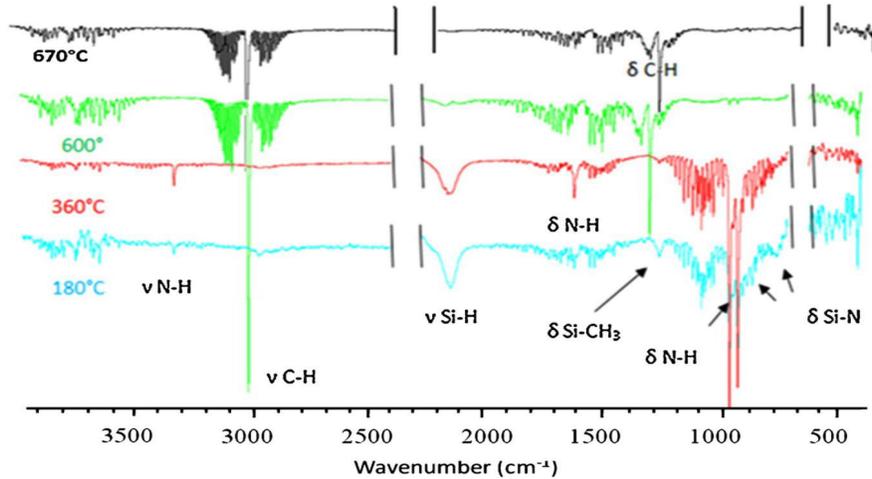


Figure 2

While some pyrolysis protocols can exceed 1000°C for special applications, there is little mass loss at such temperatures, and heating to 1,400°C or beyond is typically only done when

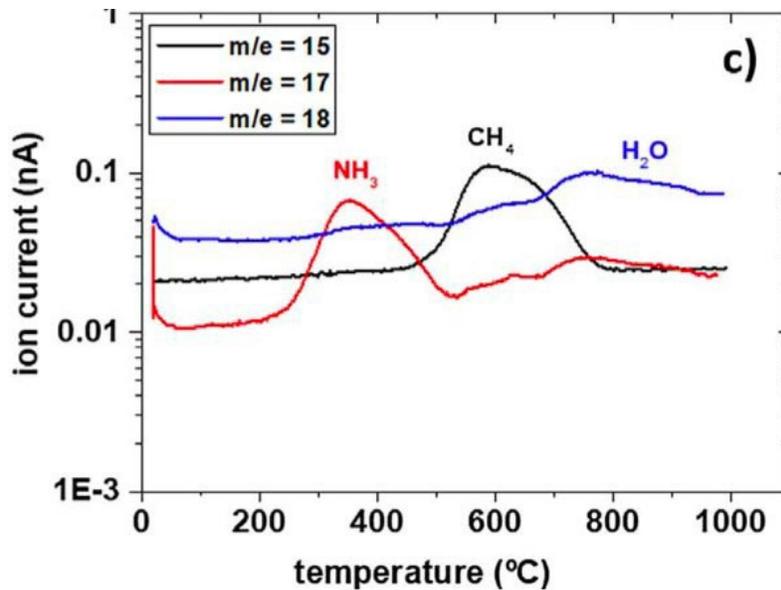
crystallization of the ceramic that is obtained is desired. Specialized annealing protocols can also be employed to modulate stress in the part if necessary.

An FTIR and Mass Spectrometric measurement of off-gassing during pyrolysis supports the above analysis and is shown in Figure 3 [B. Gardelle, S. Duquesne, C. Vu., S. Bourbigot in “Thermal degradation and fire performance of polysilazane-based coatings”, *Thermochimica Acta*, 519 (2011), 28-37] and Figure 4 [B. Roman-Manso, J.J. Moyano, D. Perez-Coll, M. Belmonte, P. Miranzo in “Polymer-derived ceramic/graphene oxide architected composite with high electrical conductivity and enhanced thermal resistance”, *J. Eur. Ceram. Soc.*, 38 (2018), 2265-2271].



FTIR Spectra of the Gases Evolved upon Pyrolysis at 180°C, 360°C, and 600°C

Figure 3

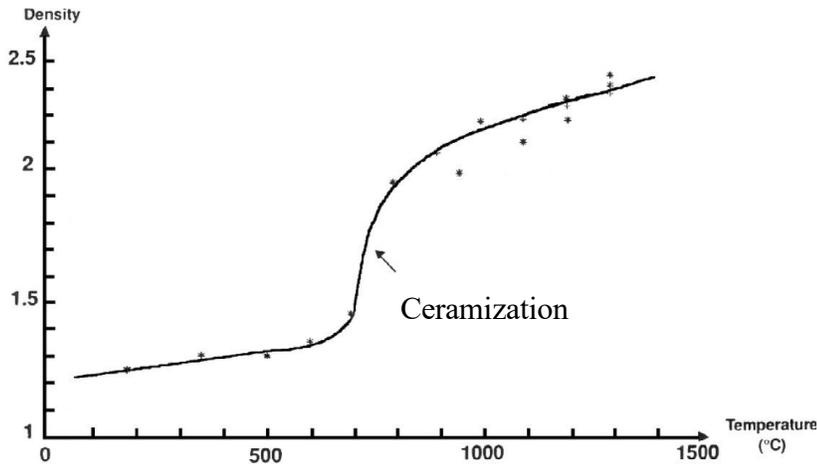


Mass Spectrum of the Gases Evolved upon Pyrolysis to 1,000°C of a Polysilazane/Graphene Oxide Composite

Figure 4

Again, a preponderance of the evolved ions in the off-gas generated in the temperature regime between 300 °C and 450 °C that are characteristic of the ammonia gas by-product expected for the transamination rearrangement. At temperatures higher than 500 °C to about 750 °C there is a preponderance of evolved ions characteristic of methane and other low molecular weight hydrocarbons evolution is observed. Concurrent with methane evolution in the temperature regime of 500 °C to about 750 °C is the evolution of hydrogen gas, which continues at temperatures up to about 900 °C. It is at these higher temperatures of about 500 °C upward that the organopolysilazane starts to form ceramic material. Until that temperature it retains its polymeric characteristics but becomes progressively more crosslinked as transamination rearrangement reactions occur and ammonia gas is evolved.

Further indication of the onset of ceramization is evidenced by density measurements of organopolysilazane materials that are heated to different temperatures, with full ceramization as shown in Figure 5.



Change in Density versus Pyrolysis Temperature for a Polysilazane

Figure 5

Ceramization is accompanied by linear shrinkage in the part as shown in Figure 6.

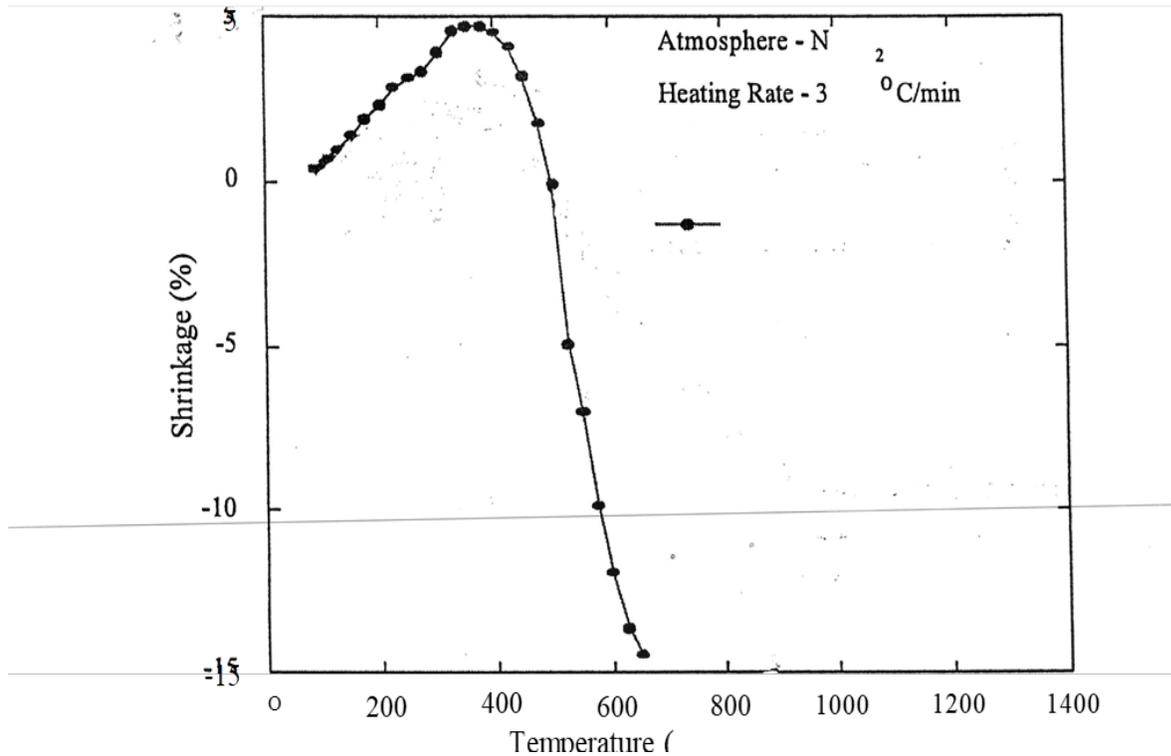


Figure 6 – Linear Shrinkage upon Pyrolysis

PART 3: Pyrolysis Ramp Rate

Generally speaking, pyrolysis is performed in a furnace with a specified rate of temperature increase, as well as selective holds at specific temperatures (ramps and soaks), designed to optimize the conversion of the material to the desired ceramic.

Pyrolysis is a very application-specific component of ceramic processing. The best pyrolysis program should be determined based on several rounds of testing, but typically,

“holds” are programmed to coincide with temperatures of peak mass loss – so as to not cause cracking of the part due to evolved pyrolysis off-gasing -- and at a temperature that “anticipates” that at which completion of mass loss is observed. Based on mass losses observed in TGA's obtained for typical polysilazanes, a useful pyrolysis protocol is provided in the table given below:

| Stage | Ramp Rate, °C/min | Hold Temperature, °C | Hold Time, Hr |
|-------|-------------------|----------------------|---------------|
| 1 | 5 | 250 | 1 |
| 2 | 10 | 450 | 2 |
| 3 | 10 | 750 | 2 |
| 4 | 10 | 1000 | 1 |

Note: Hold times are heavily dependent on total mass and surface area of the part.

PART 4: Choice of Ceramic Composition Upon Pyrolysis

In addition to the temperature profile of the pyrolysis process, the atmosphere also plays a crucial role in determining the ceramic that is formed from the polysilazane. Pyrolysis of polysilazanes in air, nitrogen, ammonia, and argon are most common. As the pyrolysis atmosphere of native (non-seeded) polysilazane changes, so does the type and phase of silicon-containing ceramic. Some of the most common atmospheres and the ceramics that are formed by pyrolyzing in those atmospheres are listed in the table below:

| Pyrolysis Atmosphere | Composition | Crystalline Phase |
|----------------------|------------------------------------|------------------------------------------------------------------------------------|
| Ar | SiC | β -SiC |
| N ₂ | SiC/Si ₃ N ₄ | α -Si ₃ N ₄ , β -Si ₃ N ₄ |
| NH ₃ | Si ₃ N ₄ | α -Si ₃ N ₄ , β -Si ₃ N ₄ |
| Air | SiC#N#O#/SiO ₂ | α -SiO ₂ , α -Si ₃ N ₄ |

Below is a comparative list of typical physical properties for those commonly generated ceramic materials.

| Property | SiCN | SiC | Si ₃ N ₄ |
|----------------------------------------------------|-----------|------|--------------------------------|
| Density, g/cm ³ | 2.35 | 3.17 | 3.19 |
| E Modulus, GPa | 80-225 | 405 | 314 |
| Poisson's Ratio | 0.17 | 0.14 | 0.24 |
| Thermal Expansion Coefficient, x10 ⁶ /K | ~3 | 3.8 | 2.5 |
| Hardness, GPa | 25 | 30 | 28 |
| Strength, MPa | 500-1,200 | 418 | 700 |
| Toughness, MPa*M ^{1/2} | 3.5 | 4-6 | 5-8 |

But In addition to temperature and atmosphere, the third, and perhaps most significant variable that contributes to which ceramic forms is filler composition. Just as in most epitaxial growth, 'seeding' with ceramic particles of a particular composition and crystalline polytype can induce conversion of the polysilazane preferentially to that composition and polytype. For example, seeding with SiC will predispose the polysilazane to convert to SiC ceramic. This will be evidenced by growth of SiC from the grain boundaries leading to a continuous ceramic phase of like composition to the seed crystal. Ceramics that can be formed using such a seeding technique include any that can form from the polysilazane feedstock polymer -- SiC, SiOC, Si₃N₄, SiOCN, etc. Fully reduced metals can also act to direct the formation of ceramics upon pyrolysis e.g. Al, B, Ti etc.

Summary:

While their popularity in industry is still limited when compared to silicones/siloxanes, the utility of polysilazanes in ceramics processing cannot be understated. As low viscosity polymers with a variety of crosslink mechanisms, high ceramic yield, and tailorable composition, polysilazanes can be exploited by most ceramic processing applications with great success. This paper is meant to provide the user with a base of understanding that will enable further optimization and confident exploration of ceramic technology using polysilazane polymers. Please contact Agostyx, LLC for more information.