

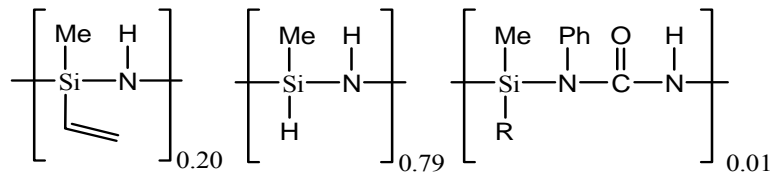


TB2: KiON[®] Ceraset[®] Polyureasilazane and KiON[®] Ceraset[®] Polysilazane 20

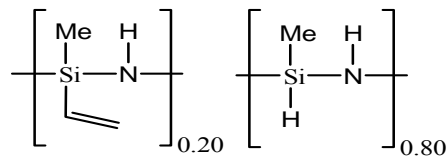
Ceramic Precursor Applications

Description:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are versatile, low viscosity liquid thermosetting resins. These patented polymers contain repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence. Both of these polysilazanes contain cyclic and linear features. The distinguishing characteristic that differentiates KiON Ceraset Polyureasilazane from KiON Ceraset Polysilazane 20 is that the former contains a small percentage of urea functionality. In addition, KiON Ceraset Polysilazane 20 contains fewer low molecular weight polysilazane components.



KiON Ceraset Polyureasilazane



KiON Ceraset Polysilazane 20

These low viscosity polymers are thermoset (cured) to a solid by heating to 180 - 200°C or at lower temperatures by adding a free radical initiator such as an organic peroxide. Alternatively, these polymers may be cured by exposure to UV radiation in the presence of a UV sensitizer. Both polymers convert to silicon carbide or silicon nitride ceramics at elevated temperatures^[1-3]. KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 were specifically designed for CMC, MMC, and other high performance ceramic precursor applications.

Uses:

- Ceramic Matrix Composites (CMCs)
- Metal Matrix Composites (MMCs)
- Corrosion Resistant Coatings
- Infiltrants for Ceramic Performs
- Oxidation Resistant Coatings
- High Temperature Coatings
- Polymer Infiltration / Pyrolysis (PIP)

Thermoset Characteristics:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are readily thermoset to a solid through a vinyl crosslinking mechanism by heating to 180-200°C. Cure can be achieved at lower temperatures through the addition of a small quantity of a free radical generator, typically a peroxide. Various types of peroxides will afford thermal cure to a solid in times ranging from 1 to 90 minutes and at temperatures ranging from 90°C (194°F) to 190°C (374°F). Please refer to *"Technical Bulletin, TBI: KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20, Heat-Curable Resins"* for a description of suitable peroxides and cure conditions. While thermal initiation of free radical crosslinking is most frequently practiced, UV, laser, and microwave cures have also been demonstrated.

Upon peroxide curing of the liquid KiON Ceraset Polysilazane based resins, a rigid solid results which is insoluble in common organic solvents, water, and dilute acids and bases. The cured solid is non-melting and does not flow or slump upon pyrolysis. The "char yield", an indication of mass conversion to ceramic material, as measured by thermal gravimetric analysis (TGA), is about 75% for KiON Ceraset Polysilazane based resins in both nitrogen and argon and about 95% in air. Figure 1 shows the TGA curves under different pyrolysis atmospheres.

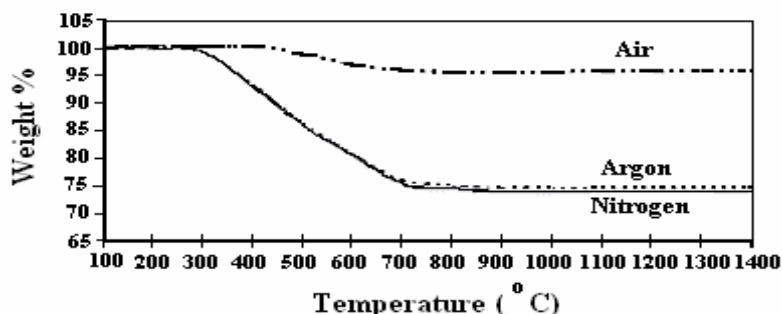


Figure 1) Thermogravimetric Analysis of Cured KiON Ceraset Polyureasilazane

Characteristics of Pyrolyzed KiON Ceraset Polysilazane Based Resins:

KiON Ceraset Polysilazanes are converted from silazane-based polymers to silicon carbonitride ceramics upon pyrolysis. The conversion from polymer to amorphous ceramic to crystalline ceramic occurs gradually as the temperature is increased. X-ray powder diffraction experiments have shown that crystallization begins above 1400°C. The final ceramic phase is dependent upon the pyrolysis atmosphere and the presence of fillers, which could act as seeds for crystallization. Evolution of crystallinity of the pyrolyzed polymer in various atmospheres is shown below in figures 2 and 3 [3].

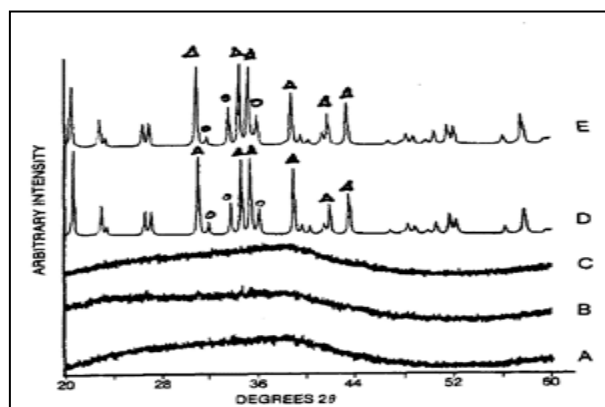


Figure 2) XRD Patterns of Polyureasilazane Pyrolyzed to; (A) 1200°C, (B) 1300°C (C) 1400°C (D) 1500°C and (E) 1600°C under Nitrogen.

(Δ) Denotes Alpha Silicon Nitride Peaks and (O) Denotes Beta Silicon Nitride Peaks.

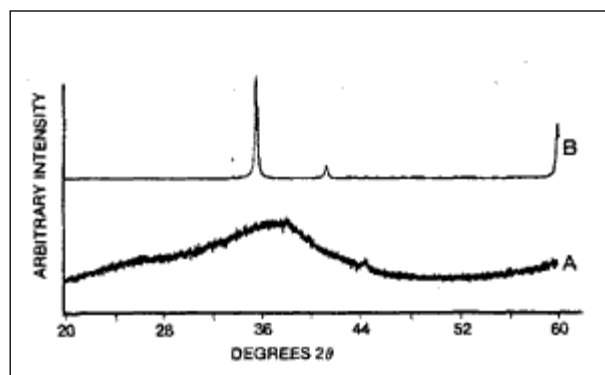


Figure 3) XRD Patterns of Polyureasilazane Pyrolyzed to (A) 1200°C, (B) 1600°C Under Argon.

Pyrolysis Composition (1600 °C) of KiON Ceraset Polysilazanes

Pyrolysis Atmosphere	Composition	Crystalline Phases
Argon	SiC	β -SiC
Nitrogen	SiC/Si ₃ N ₄	β -SiC, α -Si ₃ N ₄ , β -Si ₃ N ₄
Ammonia / Nitrogen*	Si ₃ N ₄	α -Si ₃ N ₄ , β -Si ₃ N ₄
Air**	SiC _x N _y O _z / SiO ₂	α -SiO ₂ , α -Si ₃ N ₄

*Ammonia to 800°C, then nitrogen to 1600°C.

** Pyrolysis composition very dependent upon process conditions

Influence of Crystal Seeding on Final Ceramic Phase:

Crystal seeding influences the exact crystalline phase formed; for example, pyrolysis in argon in the presence of α -SiC powder results in an α -SiC ceramic phase. Typically, crystal growth occurs epitaxially at the surface of the seed crystals. Thus, templating influences are highly dependent on surface contact and the relative amounts of polymer and seed crystal.

Influences of Crystal Seeding on Pyrolysis Composition (1600°C)

Atmosphere	Seed	Observed Pyrolyzed Phase
Ar or N ₂	α -SiC	α -SiC
Ar or N ₂	β -SiC	β -SiC
Ar or N ₂	α -Si ₃ N ₄	α -Si ₃ N ₄
Ar or N ₂	β -Si ₃ N ₄	β -Si ₃ N ₄

Ceramic Processing with KiON Ceraset Polyureasilazane:

Preceramic polymers can improve traditional ceramic processing methods. In particular, forming methods such as injection molding may be enhanced by the replacement of organic binders with thermosetting polysilazanes. A comparison of the attributes of an organic binder to a preceramic polymer binder, such as KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane 20, is tabulated below.

Ceramic Processing Comparison: Organic vs. Preceramic Polymer Binders	
Organic Binder	Preceramic Polymer Binder
Thermoplastic	Thermoset
Hot mix / Cold mold	Cold mix / Hot mold
Binder must be burned out	Binder "burns in"
High shrinkage during firing	Lower shrinkage during firing

Fillers:

The preceramic polymers are compatible with a variety of particulate or fiber fillers such as metals, ceramics, minerals or other polymers. Filled systems can be thermoset as previously described. Certain fillers may markedly reduce the bench life of the polymer/peroxide solution.

Binder:

Strong, durable green bodies can be prepared by a number of shape forming methods utilizing the thermosetting properties of KiON Ceraset Polysilazanes. Dispersion onto powders can be accomplished using traditional ceramic mixing techniques such as rolling mill, shear mixing and double planetary mixing.

Molding/Shape Forming:

The low viscosity and ease of handling of KiON Ceraset Polysilazanes in an air environment make them ideal for use as powder binders or as the carrier phase for various traditional ceramic processing techniques. Injection molding, resin transfer molding and pour molding have been used to fabricate parts using KiON Ceraset Polysilazane inorganic polymers. The preceramic polymer constituent used is typically added at about 15-20 wt%. It is usually recommended that the slurry be degassed prior to molding. Techniques requiring a "dry" powder (e.g., dry pressing and cold isostatic pressing) have also been successfully implemented to fabricate parts using low concentrations of KiON Ceraset Polysilazane inorganic polymers as a powder binder. The advantage of KiON Ceraset Polysilazanes over organic binders is that binder "burn-out" is not required, and the inorganic polymer becomes an integral part of the system. The amount of preceramic polymer required for the various processing techniques is dependent on particle composition, particle size and particle size distribution.

Tooling:

A variety of tooling materials have been used in molding parts containing KiON Ceraset Polysilazanes. These include RTV silicone rubber, aluminum, steel and fluoropolymers. Shaped articles may be directly thermoset in a heated mold. Due to the liquid nature of the thermosettable inorganic polymers, porous or rough mold surfaces present the most difficult mold sticking problems. The solid, thermoset polymers have been found to adhere to many surfaces, including numerous metals, glasses, ceramics and polymers so an appropriate release agent should be used. Conventional mold releases such as paraffin wax or silicones are most commonly used although various aerosol bake or no-bake release coatings (epoxy, polyester) have also been used successfully. Mono-Coat E179 N-ODS (Chem-Trend Incorporated) and Pd Ultra II Polyester Parfilm Mold Release (The Price-Driscoll Corporation) are examples of these systems.

Processing Examples:

Silicon Carbide - Injection Molded Green Bodies:

Silicon carbide slurries containing 20, 45 and 60 vol% SiC particulate and KiON Ceraset Polyureasilazane (0.5 wt% dicumyl peroxide initiator added to polymer) were prepared on a roll mill (without grinding media). Green flexural bars were fabricated by injecting the degassed slurry into a mold heated to 150° C. The part was cured for 1 hour at 150°C. The green flexural strength in the as-cured state (4-point bend at room temperature) is tabulated in the table below:

Composition	Green Flexural Strength (MPa) (<i>ksi</i>)
20 vol% 1200 grit SiC	20 (2.9)
45 vol% 1200 grit SiC	24 (3.5)
60 vol% SiC (60/40%: 500/1200 grit)	32 (4.6)

Silicon Nitride - Dry Pressed Green Bodies:

Silicon nitride dry press mixes were prepared by hand mixing various levels of KiON Ceraset Polyureasilazane (0.5 wt% dicumyl peroxide initiator added to polymer) with sub-micron silicon nitride powder (UBE SN-E10). Green flexural bars were fabricated in a 150°C mold by pressing at 15 ksi for 5 minutes.

Binder level wt%	Green Flexural Strength MPa (<i>ksi</i>)
2	<1.0 (<0.15)
4	1.2 (0.18)
8	8.0 (1.2)
16	12.0 (1.8)

SiC Fiber-Reinforced Composites by Polymer Infiltration and Pyrolysis:

Pyrolysis of KiON Ceraset Polysilazanes results in an increase in the material density. The density increase occurs with a volumetric decrease, which typically manifests itself as internal porosity. The volumetric reduction can be compensated for in particulate and fiber reinforced composites by subjecting the parts to a series of polymer infiltration and pyrolysis (PIP) cycles. In the PIP process, the shape stabilized preform (fiber or particulate) is infiltrated with liquid KiON Ceraset Polysilazane, cured to thermoset the polymer, then pyrolyzed to convert the polymer to ceramic.

The number of required PIP cycles will depend on the desired matrix phase (e.g.; silicon carbide, silicon nitride, ...) and pyrolysis temperature. Typically six densification cycles are required for pyrolysis at 1000°C to achieve greater than 90% theoretical density.

Nicalon® and Hi-Nicalon® fiber reinforced composites have been fabricated through a series of PIP cycles with KiON Ceraset Polysilazane. The composites were fabricated with 35-40% fiber volume as 0/90 lay-ups using a duplex carbon/silicon carbide debond layer on the fibers. Specific examples for pyrolysis in argon to give a SiC matrix or pyrolysis in ammonia to give a Si₃N₄ matrix are shown in the table below. The fiber volume can be adjusted depending upon the fabrication techniques used.

Fiber	Fiber Weave	Pyrolysis Temp (°C)	Matrix	Flex Strength MPa (ksi)
Nicalon®	8HSW	1000	SiC	404 (59)
Hi-Nicalon®	plain	1300	SiC	580 (83)
Nicalon®	8HSW	1000	Si ₃ N ₄	300 (43)

Reactivity:

KiON Ceraset Polysilazanes are liquid, polysilazane-based resins. These materials are reactive with acids, bases, alcohols, and water and will slowly produce ammonia upon contact with these substances.

Health and Safety:

KiON Ceraset Polysilazanes are listed on the EPA/TSCA (Toxic Substance Control Act) inventory of chemical substances. *Please refer to the Materials Safety Data Sheet (MSDS) for details concerning the health hazards of KiON Ceraset Polysilazane . The toxicity or other hazards of this material, alone or in combination with other substances, are not fully known. Read the health and safety information provided before using this material .* KiON Ceraset Polysilazanes have a musty amine or ammonia-like odor and should be used in fume hoods or with adequate ventilation. The material should be used with appropriate personal protective clothing, safety glasses and/or goggles and impervious gloves.

KiON Corporation Polysilazane Technical Bulletins:

TB1 “KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 - Heat-Curable Resins”

TB2 “KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 - Ceramic Precursor Applications”

TB3 “KiON Polysilazanes: Reactivity with Isocyanates”

TB4 “KiON Polysilazanes: Reactivity with Phenolic Resins”

TB5 “KiON Polysilazanes: Reactivity with Epoxy Resins”

References:

1. Ceraset and KiON are registered trademarks of KiON Corporation.
2. U.S. Patent 4,929,704; 5,001,090; 5,021,533; 5,032,649; 5,155,181; 6,329,487.
3. R.L.K. Matsumoto Mat, Res. Soc. Symp. Proc., 1990, 180, 797-800.

All information on KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 is based on experimental results. Although we believe this information to be reliable, we expressly do not represent, warrant, or guarantee accuracy, completeness, or reliability. NO REPRESENTATIONS OR WARRANTIES, EXPRESSED OR IMPLIED OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR OTHERWISE ARE MADE OR CONTAINED HEREIN. Each user should conduct a sufficient investigation to establish the suitability of any product for the intended use. User should comply with all applicable safety and environmental standards. Nothing herein is to be construed as advising or authorizing practice of any invention covered by existing patents without license from the owners thereof.

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