TB3: KiON® Polysilazanes - Reactivity with Isocyanates

Background:

KiON Polysilazanes are patented polymers which contain repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence. The majority of KiON Polysilazanes are low viscosity liquids. KiON Polysilazanes all possess reactive Si-N functionality which enables co-reaction with various organic resins such as epoxies, isocyanates, and phenols [3].

Applications:

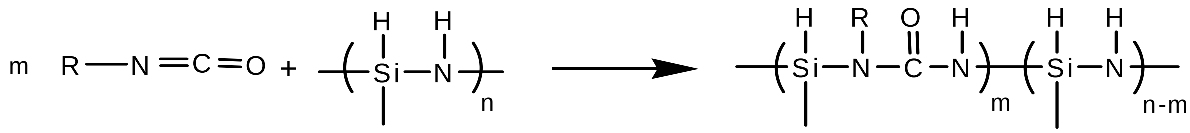
In general, polyisocyanates cured with KiON Polysilazanes will display greater hardness, higher modulus, higher strength, and lower elongation than polyol cured polyisocyanates. These inorganic / organic hybrid polyurea systems offer a broad range of properties useful in a variety of applications.

Uses:

- rigid cast objects
- glass fiber-reinforced composites
- coatings
- adhesives
- cast elastomers

Isocyanate Reactivity:

The reaction of silazanes with organic aromatic isocyanates is rapid and highly exothermic at room temperature, and occurs via a mechanism which involves addition of Si-N bonds, rather than N-H bonds, across the C=N bond of the isocyanate group. The reaction of silazanes with organic aliphatic isocyanates is more moderate and, depending on the isocyanate used, may require modest heating to effect complete reaction. When monofunctional isocyanates are employed for the modification of polysilazanes, the resulting product is a polyureasilazane:



Multifunctional isocyanates react in an analogous fashion to monofunctional isocyanates, in this case to form crosslinked structures directly from the reaction of the Si-N bonds in the polysilazanes with the isocyanate groups. Such reactivity can be used to formulate two-part thermoset systems which can be used directly, or in combination with a filler.

As with two part polyurethane resins, the reactivity of liquid polysilazanes with aryl isocyanates is quite pronounced and rapid at room temperature. Caution should always be exercised when such systems are formulated, as the exothermic nature of the cure can generate significant heat. Since each application is unique, safe operating procedures must be determined by the individual user. Two part systems based on the reaction of aryl polyisocyanates with a polysilazane typically include a filler to ameliorate the thermal effects of the exothermic cure.

In general, aromatic isocyanates react rapidly at room temperature with KiON Polysilazanes with gel times in particle-filled systems of about 3-15 minutes. Aliphatic isocyanates typically require several hours at room temperature prior to gellation and solidification. Curing can be accelerated by heat.

Characteristics of Cured Systems:

Incorporation of KiON Polysilazanes into the resin system imparts improved thermal performance and retention of mechanical properties to higher temperatures than for conventional polyurethane or polyurea systems.

The TGA curves for methylenediphenyl diisocyanate (MDI) cured with 1,4-butanediol and with KiON CERASETpolyureasilazane are shown in Figure 1. Each sample contained 80wt% MDI and 20wt% hardener. The data was obtained in nitrogen to 800°C.

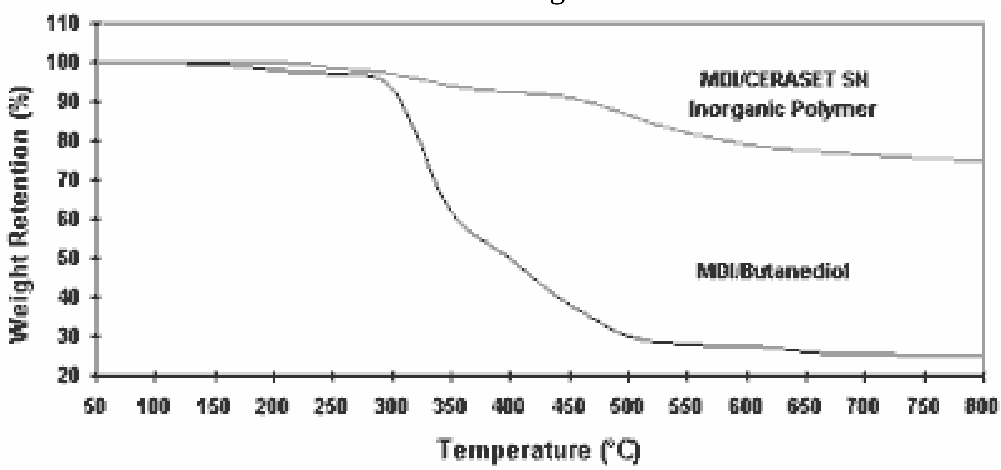


Figure 1. TGA Data in Nitrogen for MDI/KiON Ceraset Polyureasilazane Hybrid Polymer

The relative tensile properties of a commercial MDI-based casting resin and a MDI/KiON Ceraset Polyureasilazane casting resin are shown in Figure 2. Both systems were cast at room temperature and post cured. Tensile strength of the polyol-based system could not be measured above 50°C. The KiON Ceraset Polyureasilazane hybrid polymer system displayed twice the tensile strength of the MDI control.

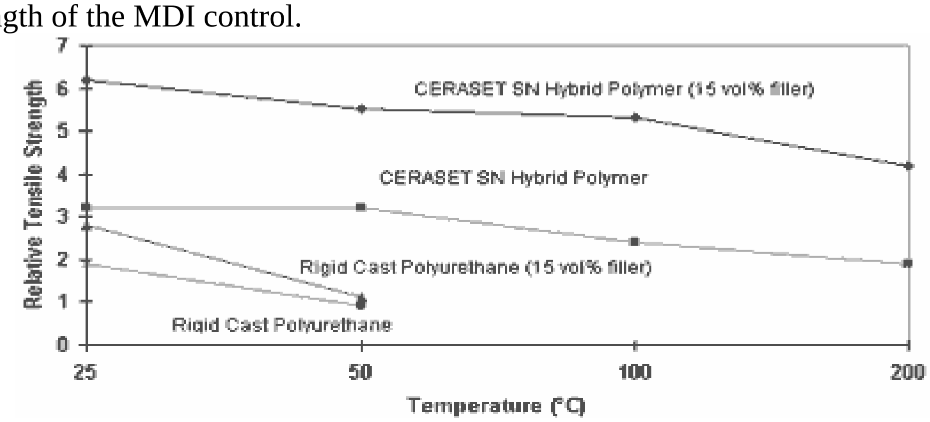


Figure 2. Relative Tensile Strength vs. Temperature

Molding Applications:

The materials provide excellent reproduction of detail. The resins can be used with a wide range of processing techniques including resin transfer molding (RTM), conventional casting, vacuum infiltration, vacuum bagging, and reaction injection molding (RIM).

The hybrid polyurea resins have been used in a range of applications including coatings, adhesives, casting resins, glass fiber-reinforced composites, and flooring for heavy traffic and wear areas.

Representative Formulations and Properties:

The amine equivalent weight of various KiON Polysilazanes depends on the exact resin which is used to prepare the polysilazane. While the Si-N repeat units in KiON Polysilazanes generally have molecular weights approximating 70 g/mol, experience has shown that not every Si-N bond reacts in the formation of the hybrid polymer. Representative resin ratios for aromatic and aliphatic isocyanate systems are indicated below. Examples of formulation with various fillers and typical physical properties follow. Not all of the process conditions are optimized.

The aromatic isocyanate-containing formulations react rapidly and exothermically at room temperature with gel times in particle-filled systems of about 3-15 minutes. We do not recommend using the aromatic isocyanate-containing resins without a filler which acts as a heat sink for the exotherm generated during the cure. Aliphatic isocyanates typically require several hours at room temperature prior to gellation and solidification. Curing can be accelerated by heat.

Polysilazane/Isocyanate Resin System Examples:

A) Aromatic MDI system

80 parts by weight methylenediphenyl diisocyanate (MDI)
20 parts by weight KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane 20

B) Aromatic MDI/Polyether TDI system

60 parts by weight methylenediphenyl diisocyanate (MDI)
20 parts by weight toluene diisocyanate (TDI) terminated polyether
20 parts by weight KiON Ceraset Polyureasilazane or KiON
Ceraset Polysilazane 20

C) Aliphatic isocyanate (HDI trimer) system

75 parts by weight hexamethylenediisocyanate trimer
25 parts by weight KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane 20

Example 1. Particulate-filled MDI / KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane 20 polymer casting resin.

The MDI and TDI-terminated polyether (resin system "B") above are stirred together to form a homogeneous mixture. Silicon carbide powder (15 volume %) is blended into the isocyanate mixture. The formulation is degassed under vacuum. The KiON polysilazane is added to the degassed formulation and carefully mixed by hand to minimize entrapment of air. Caution: the bench life of this mixture is only 2-4 minutes at room temperature depending upon the volume of material. The curing process is extremely exothermic. Parts should be limited to a maximum thickness of about 1 inch. The resin is cast into a mold at room temperature, demolded after 7-10 minutes, and post-cured at 125°C for 12 hours. Properties of example systems are tabulated below.

Filler	Filler (Vol%)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Hardness Rockwell M
ZrO_2	4	67	2.7	110
SiC	15	62	3.6	110
WC	14	56	3.7	92

Example 2. HDI trimer / KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane 20 polymer hybrid composite.

A casting resin mix is prepared by blending the two resins of (C), on previous page, (40 parts by weight) with a dry mix of alumina powder and alumina trihydrate powder (60 parts by weight). Slow mixing will minimize air entrapment. Optionally pigment and various additive packages may be added. The resin is poured or injected into a mold (treated with mold release) containing random glass mat and cured under pressure at 135°C for 3 minutes.

Test Method	ASTM C293	ASTM E84	ASTM E84	ASTM D658	
Test	Flexural Strength (MPa)	Flame Spread Index	Smoke Density	Abrasion (inches/60 s)	Tg (°C)
Results	178	20	105	0.0058	77

Note: In addition the composite passed chemical resistance (ASTM D-1308), freeze/thaw/heat cycles (ASTM C-1026), and stain resistance (ASTM D-2299).

Example 3. HDI trimer/ KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane polymer hybrid glass fiber composite.

The two resins of (C), on previous page, were mixed and degassed under vacuum and fabricated into a glass fiber-reinforced composite using a vacuum bag /autoclave process. Each panel contained 7 plies of glass in a 0/90 lay-up. The samples were cured in an autoclave at 85 psi and 125°C for 2 hours. The physical properties for two glass fiber types are tabulated below.

Glass fiber	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Strain to Failure (%)
E-glass	384	20.3	402	2.1
S-glass	584	28.3	572	2.1

Example 4. HDI trimer / KiON Ceraset Polyureasilazane or KiON Ceraset Polysilazane polymer hybrid adhesive.

The two resins of ©, on previous page, were mixed and degassed under vacuum and applied to metal surfaces to be joined. The adhesive, after curing to 120°C, showed a shear strength of 18.3 MPa and an elongation of 10.7%.

Handling and Storage:

The neat liquid polysilazane should be stored in a closed plastic or metal container at or below room temperature to maximize shelf life. Under these conditions the shelf life of the polymer is in two years. Material in unopened original containers has been show to be viable up to five years. Once combined with an isocyanate the pot life will be strongly dependent upon the ambient temperature and the type of isocyanate employed. Due to the potential exothermic nature of polysilazane/isocyanate mixtures small quantities (10 to 100g) should be prepared to determine reaction conditions before proceeding to any large scale operations.

Health and Safety:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 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 Polyureasilazane and KiON Ceraset Polysilazane 20. 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 Polyureasilazane and KiON Ceraset Polysilazane 20. These polysilazanes have a musty amine or ammonia-like odor and should be used in a fume hood 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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