

## **TB5: KiON<sup>®</sup> Polysilazanes - Reactivity with Epoxy Resins**

### **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].

### **Basic Epoxy Reactivity:**

Although silazanes are formally disilylamines, their reactivity with epoxies does not parallel that of organic amines. Silazanes are not as basic as organic amines, and the reactivity of silazane-based polymers with epoxy resins stems primarily from the polarity of the Si-N bond and its reactivity with active hydroxyl functionality resulting from epoxy ring opening reactions. For example, stoichiometric quantities of KiON Polysilazanes can be reacted with epoxy resins based on the diglycidyl ether of Bisphenol "A" to give "cured" resin systems. Assuming exhaustive reactivity for the Si-N bonds in a KiON polysilazane, the "amine" equivalent for these polymers would be about 70 g/eq. This value, however, can only be considered a guideline for formulation, since the fraction of Si-N bonds in a KiON Polysilazane which react with any given epoxy resin varies from resin to resin. Ambient temperature shelf stability in excess of six months for such dual component systems has been observed.

Epoxy resin cure using KiON polysilazanes can be achieved under pressure (autoclave curing) by heating initially to 100°C for at least 2 hours (7°C / minute ramp) followed by a post-cure for several hours (12 hours) at >165°C. Cure or postcure temperatures of as high as 260°C have been used provided sufficient "pre-reaction" time at 100 °C is allowed. Compositions containing high percentages of Bisphenol "A" diglycidyl ether epoxy resin were found to undergo phase separation during cure, while compositions high in KiON polysilazanes [> 65 wt%] were rather brittle. Sample formulations are shown below. [Please note, however, that none of these systems have been optimized for stoichiometry or cure schedule. The observations described should be used only as guidelines.] Our experience has shown that catalysts such as the N,N-disubstituted anilines such as the Ancamine<sup>®</sup> catalysts [e.g. Ancamine<sup>®</sup> K54 tris(dimethylaminophenol)] or Lewis Acids are not desirable for the reaction of epoxy resins with KiON polysilazanes, since they promote extensive foaming at temperatures lower than the "pre-reaction" temperature (100 °C).

### **Epoxy Side Reactions:**

The reactivity of the Si-N bond with active hydroxyl groups creates an inherent complication when silazane-based polymers are used as hardeners for epoxy resins. As described above, oxirane ring opening generates free hydroxyl groups which react with (Si-N) bonds to form Si-O-C bonds in the reaction mixture. In the process of this reaction, terminal Si-NH<sub>2</sub> groups are formed within the KiON Polysilazane. Such groups can then further react with either Si-NH-Si

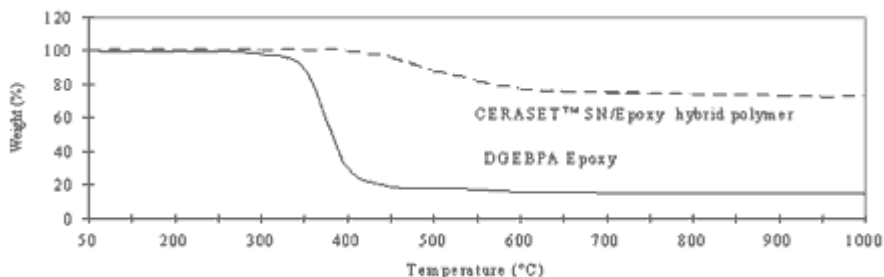
groups or other hydroxyl groups present in the reaction mixture to generate free ammonia, which is evolved during the cure.

We have found, however, that these side reactions can be ameliorated in several ways: (1) by allowing extended "pre-reaction" time at 100 °C before heating to cure temperature, (2) by performing the cure in an autoclave, (3) by using a vinyl-containing KiON polysilazane (such as KiON Ceraset Polysilazane 20) to promote vinyl crosslinking before cure [In this method a peroxide initiator which has a decomposition half-life of less than 10 minutes at the cure temperature (e.g. Elf Atochem's Lupersol® 256 or Lupersol® 231) is employed], or (4) by a combination of the above.

By using such cure techniques we have generated continuous glass fiber-reinforced composite laminates which demonstrate high hardness (115 Rockwell "M"), excellent flexural and tensile strengths, and outstanding thermal stability (see following table). This resin system and cure conditions are listed as dual component system A in the representative formulations section on page 4.

<b>S-2 Glass Fabric/Epoxy-KiON Polysilazane Hybrid Composite Properties</b>	
<b>Test Conditions</b>	<b>Retained Flex Strength (ksi Mpa)</b>
As fabricated	66 (465)
2 hour water boil	70 (490)
48 hours @ 480°F	31 (215)
24 hour water boil	0.7% weight gain
<b>Temperature</b>	<b>Tensile Strength @ Temp. (ksi MPa)</b>
25°C	127 (873)
150°C	117 (811)
300°C	110 (760)
400°C	103 (710)
500°C	42 (291)
<b>Continuous use @ 30 ksi, 400°F</b>	<b>100 hours</b>

The decomposition characteristics of such resin systems at progressively higher temperatures demonstrate the synergism of incorporating an "inorganic" polysilazane "hardener" into a conventional epoxy system. Thermal performance windows are extended toward higher temperatures, decomposition pathways are gradual, and char formation is dramatically enhanced (see attached TGA). In applications where cured resin systems having a higher degree of toughness are desirable, straight-chain aliphatic epoxy diluents can be employed (C 8 / C 10 hydrocarbon substitution).



The mechanical properties data for several unoptimized carbon fiber / KiON epoxy hybrid polymer-reinforced composites are also shown below.

### Short Beam Shear

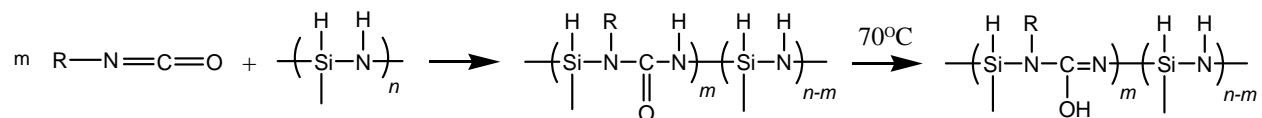
Fiber	Fiber Vol.	Standard Resin (published values)	KiON hybrid resin
AS4 / 12k	62%	17.5 ksi (121 MPa)	7.4 ksi (51 MPa)
AS4 / 3k	62%	17.5 ksi (121 MPa)	7.9 ksi (54 MPa)
AS4 / 8H	62%	9.0 ksi (62 MPa)	4.5 ksi (31 MPa)

### Tensile Strength

Fiber	Fiber Vol.	Standard Resin (published values)	KiON hybrid resin
AS4 / 12k	62%	225 ksi (1550 MPa)	192 ksi (1323 MPa)
AS4 / 3k	62%	225 ksi (1550 MPa)	167 ksi (1151 MPa)
AS4 / 8H	62%	120 ksi (827 MPa)	94 ksi (648 MPa)

### Isocyanate Modifications:

Another approach has exploited the pronounced reactivity of the Si-N bond with organic isocyanates. Isocyanates insert readily across the Si-N bonds of silazane-based polymers at temperatures slightly above ambient to generate urea segments in the polymer chain. When such urea segments contain active N-H bonds, rapid isomerization to the iso-urea configuration is observed at temperatures above about 70°C (Equation 1).



Equation 1

This isomerization generates active hydroxyl functionality which can react with oxirane rings. Thus, a three-component resin system consisting of KiON CERASET Polysilazane 20, Bisphenol "A" diglycidyl ether, and isophorone diisocyanate reacts readily at 100°C with a post-cure at > 165°C to yield a cured system without foaming.

Such three-component systems have limited shelf stability, since the reaction of the isocyanate component with KiON polysilazanes advances at room temperature. Gelation will occur over time. To circumvent these problems, especially when such compositions are being used in coating applications, blocked isocyanates are used.

## Amine Modifications:

A second alternative involves the use of KiON Polysilazane-modified amine hardeners. Conventional amine hardeners for epoxy resins can be heated in the presence of 20-25wt% of a KiON polysilazane to prepare a KiON-modified hardener. In this method the organic amine reacts with the KiON polysilazane at the Si-N bonds of the silazane-based polymers at temperatures of about 90°C to incorporate the polysilazane into the amine system. Pronounced foaming is observed at the reaction proceeds. When gas evolution subsides, the reaction is complete. Epoxy cure can be effected by adding the modified-amine hardener to the epoxy resin at proportionately higher amounts than recommended by the manufacturer (i.e. compensating for the total mass of polysilazane added). While this method works very well for a variety of amine hardeners, polyamide hardeners are not suited to this method.

## Representative Formulations:

Listed below are three formulations with representative curing schedules (not optimized). We have also cured epoxy compositions at higher temperatures (up to 260°C for 1-2 minutes for coatings and thin films).

### A) Dual Component System (can be used as a 1 part resin system)

**60 grams** KiON Ceraset Polysilazane 20 and **40 grams** Bisphenol "A" diglycidyl ether

**6 grams** Lupersol® 256 2,5-dimethyl-2,5-di-(2-ethylhexanoyl-peroxy)hexane (Elf Atochem)

Blend all three components. Cure in air at 100°C for 2 hours (7° C / minute ramp from ambient temperature). Post-cure at > 165°C for 12 hours. Cure is best achieved in an autoclave.

### B) Two Part System (Part A + Part B)

<b>Part A: 60 grams</b> KiON Ceraset Polysilazane 20 and <b>10 grams</b> Isophorone diisocyanate	<b>Part B: 40 grams</b> Bisphenol "A" diglycidyl ether
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**Initiator (optional)** 0.8 grams Lupersol® 256 2,5-dimethyl-2,5-di-(2-ethylhexanoyl-peroxy)hexane (Elf Atochem) can be added to impart enhanced compositional homogeneity.

For immediate use, blend initiator (if desired) with part A, and then add Part B. Cure in air at 100°C for 2 hours. Post-cure at > 165°C for 12 hours.

### C) One Part System (using a blocked isocyanate)

**16 grams** KiON Ceraset Polysilazane 20, **42 grams** Bisphenol "A" diglycidyl ether and **54 grams** Luxate® HC 1170 blocked hexamethylene diisocyanate trimer. (Olin: 70wt% solids in butyl acetate)

**Initiator (optional): 0.5 grams** DiCup® bis(tert-butylperoxy)diisopropylbenzene can be added to impart enhanced compositional homogeneity

Blend all four components (including initiator, if desired). Cure in air at 100°C for 2 hours. Post-cure at > 165°C for 12 hours.

**Storage:**

The liquid polymer 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 shown to be viable up to five years. Once mixed with a peroxide curing initiator the shelf life will be strongly dependent upon the half-life of the peroxide employed.

**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; 6,756,469.
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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