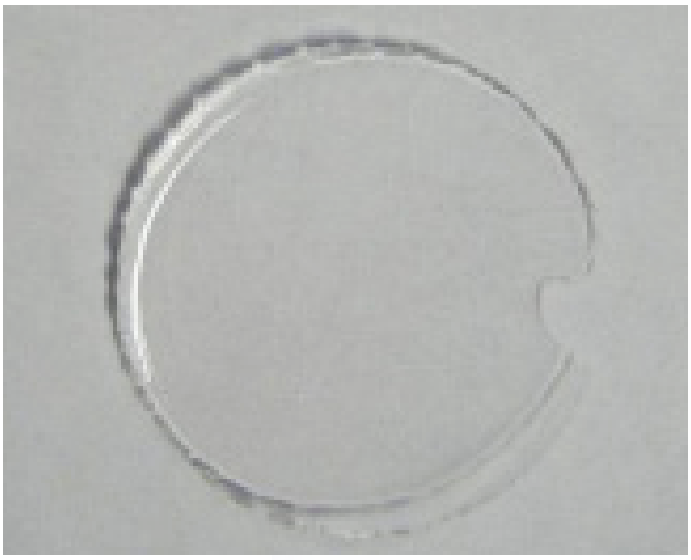
STARFIRE SYSTEMS

POLYMER-TO-CERAMIC™ TECHNOLOGY

POLYRAMIC® RESINS BROCHURE

Inorganic polymers for flame resistant and pre-ceramic applications

INTRODUCTION TO POLYRAMIC RESINS®



Cured Polyramic® part

Polyramic® resins are a family of inorganic polymers with organic functionality based on a siliconoxygen backbone. They are liquid resins which are cured to transparent thermoset polymer parts with a controllable degree of cross-linking. Certain Polyramic® resin compositions can be further heated to high temperature (greater than 600°C) to yield silicon oxycarbide ceramics. Polyramic® resins are especially noted for their:

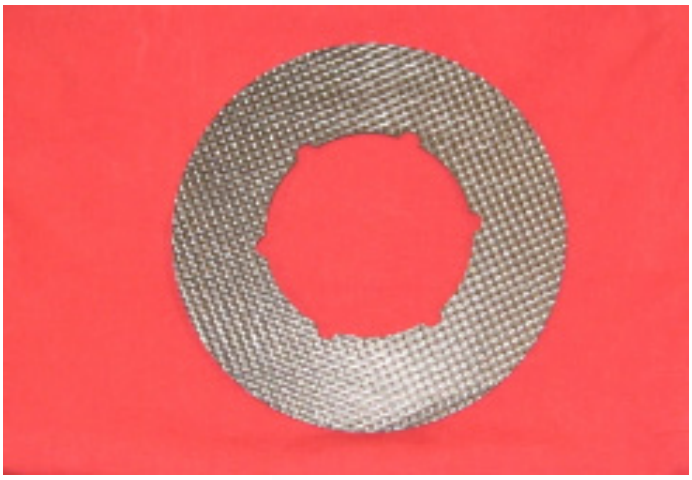
- **Ease of processing:**
  Liquid resins which can be pre-pregged, cast, and infiltrated to yield polymers, filled polymers, polymer matrix composites and ceramic matrix composites (CMCs).

- **Inherent fire resistance:**
  The cured resins are fire resistant without other additives.

- **Low dielectric constant and low dielectric loss:**
  Up to 10GHz – in the cured polymer state.

- **Ceramic forming ability:**
  Can be pyrolyzed to yield silicon oxycarbide ceramics with excellent high temperature oxidation stability; up to 1400°C for short periods of time. Polyramic® resins are available in a wide range of viscosities, which suits any application, and can be cured with free-radical initiators (dicumyl peroxide) or by hydrosilylation catalyzed by low levels of precious metals, such as platinum.

THE POLYRAMIC® FAMILY



Polyramic® resin 2D CMC Laminate

The Polyramic® family consists of a variety of compositions, each with unique properties. All Polyramic® resins contain a certain amount of vinyl and hydride (Si-H) functionality in addition to other functional groups that do not participate in crosslinking but provide other properties; toughness in the cure state and control over free carbon content in the pyrolyzed state.

- SPR-684

  SPR-684 was originally developed for electronic laminate applications. It is typically used in its cured polymeric state. It can be pyrolyzed to yield a silicon oxycarbide ceramic but has poor oxidation stability in this state.

- SPR-688

  SPR-688 is also typically used in its polymeric state where it is most notable for its exceptional flame resistance. However, in combination with SPR-212 it is also very useful as a pre-ceramic polymer for CMC applications. It forms a stable green body in its cured form after treatment to moderate temperature which allows for ease of handling prior to full pyrolysis.

- SPR-212

  SPR-212 is most useful as a silicon oxycarbide former. It has high ceramic yield, low viscosity and excellent oxidation resistance in the pyrolyzed state. Its low viscosity makes it an ideal infiltrating polymer.

- SPR-036

  SPR-036 is a silicon oxycarbide former with less organic functionality than SPR-212. It has similar properties to SPR-212 but may provide additional strength in certain applications.

PROPERTIES OF THE LIQUID RESINS

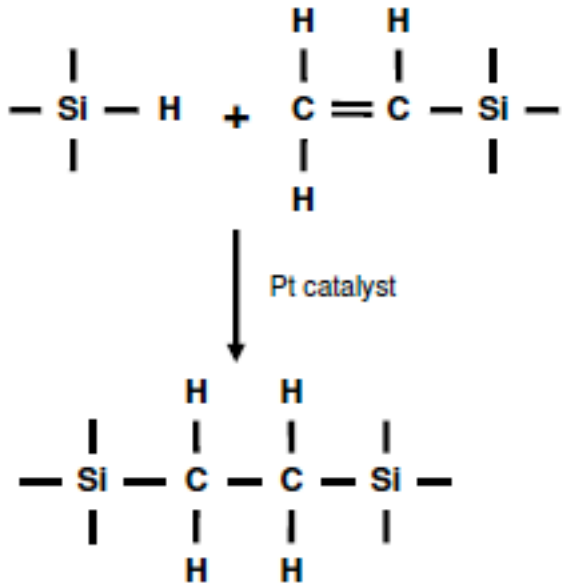
Polyramic® resins are liquid resins typically ranging from water-clear to milky or opaque. Available viscosities range from below 20 cP to over 10,000 cP depending on composition and desired application. Liquid resins have a minimum shelf life of 6 months with most remaining stable for 12 months with room temperature storage.

Resin	Viscosity (cP)	Density (g/cm^3)	Solvents	Flash point (°C)
SPR-684	3,000 – 8,000	1.2	Toluene, Xylene, Hexane, THF, Acetone, MEK	>93
SPR-688	300 – 2,000	1.1	Toluene, Xylene, Hexane, THF	>93
SPR-212	12 - 26	1.0	Hexanes, THF, Toluene, Xylene	62
SPR-036	50 - 500	1.1	Hexanes, THF, Toluene, Xylene	56

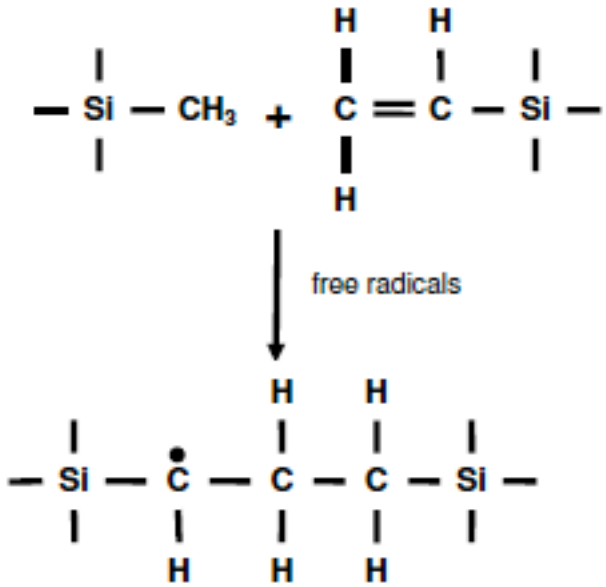
Properties of the Polyramic® liquid resins.

CURING AND PYROLYSIS OF POLYRAMIC® RESINS

Polyramic® resins can be cured with either hydrosilylation catalysts, typically platinum complexes, or with free-radical initiators such as organic peroxides. The most appropriate catalyst will depend on the manufacturing process. For example, Polyramic®/glass fabric laminates may be produced by first making pre-preg and then pressing to form a laminate. For this application hydrosilylation catalysts, such as platinum are most appropriate due to the ease of stopping the reaction part way through to pre-preg and then restarting the reaction to go to full cure during pressing (lamination). Organic peroxides, and other freeradical initiators, on the other hand, are useful when a rapid cure at a fixed temperature is required. Free-radical initiators are available which initiate reactions at different given temperatures which allows for flexibility in setting the cure cycle and optimizing for a given application.



Cross-linking via platinum catalyzed hydrosilylation



Free-radical initiated cross-linking

VARIOUS CATALYSTS AND INITIATORS

Catalyst/Initiator	Type	CAS	Comments
Platinum (0) -1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex	Hydrosilylation	68478-92-2	Typically used either in xylene or a solution of the complexing agent at a 0.2 wt% Pt concentration.
Dicumyl peroxide	Free-radical	80-43-3	Typically used as 50 wt% solution in toluene.
Di-*tert*-butyl peroxide	Free-radical	110-05-4	
Cumene hydroperoxide	Free-radical	80-15-9	
Benzoyl peroxide	Free-radical	94-36-0	Water in benzoyl peroxide can cause problems in higher Si-H containing polymers.
Azobisisobutyronitrile (AIBN)	Free-radical	78-67-1	Typically used as 15 wt% solution in tetrahydrofuran
1,1'-Azobis(cyclohexanecarbonitrile) (ABCN)	Free-radical	2094-98-6	Typically used as 15 wt% solution in tetrahydrofuran

Typical curing schedules

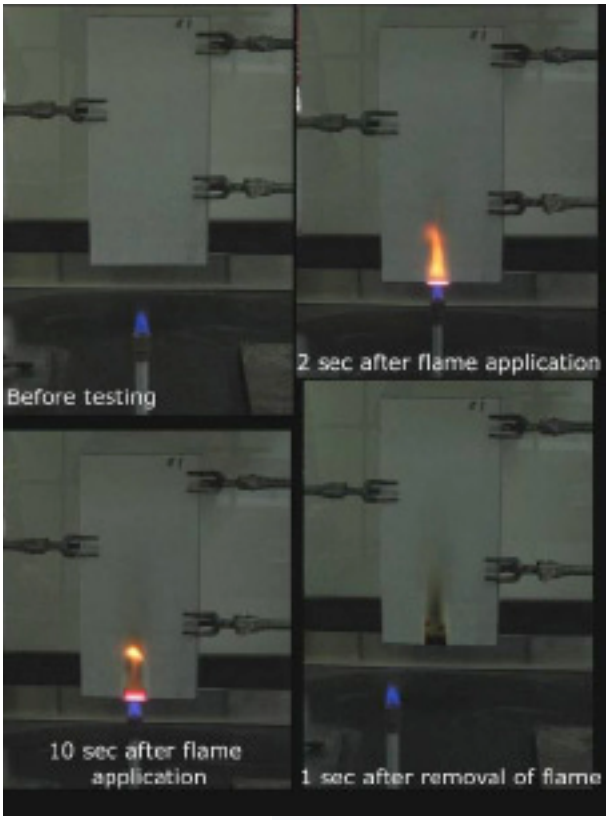
For curing with platinum, a typical curing schedule consists of a ramp to 300°C at up to 10°C/min followed by a hold of at least 30 minutes. The minimum curing temperature is 120°C. Curing temperature and part geometry will dictate the necessary hold time to achieve full cure. Peroxides will typically cure in the range of 160 to 200°C, although benzoyl peroxide can effect partial cure at 130°C. AIBN and ABCN will facilitate cure in the 120 to 150°C range.

Typical pyrolysis schedules†

Temperatures over 850°C will result in pyrolyzed ceramic parts. Ramp rates of 1 to 5°C/min will minimize defects due to shrinkage and outgassing. Complex geometries, thick cross-sections or high polymer content pieces will typically require holds at strategic temperatures to achieve solid parts. Use of catalysts will improve the pyrolysis yield which ranges from 65 to 85% depending on conditions and polymer composition.

†All pyrolysis should be performed in an inert atmosphere with sufficient exhaust to prevent gas buildup in the furnace.

CURED POLYMER FORMERS - SPR-684 AND SPR-688



Vertical burn Bunsen burner test on SPR-688/glass fiber composite panel.

SPR-684 and SPR-688 contain significant amounts of organic functionality. These groups result in a cured polymer that is tough and rigid but also significant free-carbon content in the ceramic state which makes them susceptible to oxidation at elevated temperatures. As such these Polyramic® resins variants are generally recommended for use in their cured polymeric state.

Fire resistance

Cured SPR-688 and SPR-684 show excellent fire resistance in glass-fiber laminate panels. SPR-684 electronic laminate was shown to be UL94 V-0 during testing.

Electronics applications

Property	Value
Dielectric constant (1.5 GHz)	3.5 – 4.2
Dielectric loss factor (1.5 GHz)	0.005 – 0.01
Thermal conductivity	0.29 W/m-K
X, Y CTE ppm/°C	5 – 15
Z CTE ppm/°C	37 – 100

SPR-684 was originally conceived as an electronic laminate material for high frequency applications.

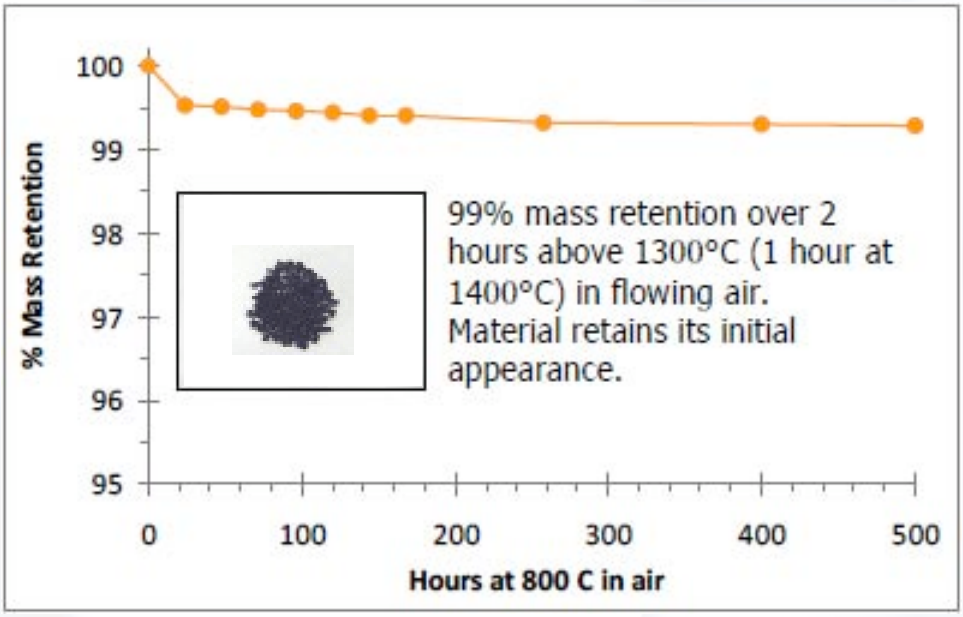
CMC 2-D laminate base

Parameter	C-SiOC	C-SiC
Slurry	SPR-688	SMP-10
PIP polymer	SPR-212	SMP-10
Flex strength	262 MPa	276 MPa
Flex modulus	76 GPa	76 GPa

Comparison of carbon-fiber reinforced CMC properties for Polyramic® resins and a SiC forming polymer.

SPR-688 is advantageous as a base resin for 2-D CMCs as it cures to a tough form that can withstand handling prior to pyrolysis. Although its elevated temperature oxidation stability generally makes it unsuitable for CMC applications it can be protected by subsequent infiltrations of SPR-212 which has excellent high temperature oxidation stability in its ceramic form.

SILICON OXYCARBIDE FORMERS – SPR-212 AND SPR-036



Oxidation stability of pyrolyzed SPR-212

SPR-212 and SPR-036 contain less organic functionality than the other Polyramic® resins and, as such, form highly oxidation resistance ceramic parts. SPR-212 in combination with SPR-688 is an excellent matrix-former for carbon reinforced CMCs (see data on left)

To learn more about the advantages of Polyramic® Resins for your applications please contact StarfireSystems® at:
E-mail: info@starfiresystems.com or Phone: 518-899-9336

Warranty

The data provided relates only to Polyramic® resins, as supplied by Starfire Systems, Inc. (SSI). Because conditions and methods of use of our products are beyond our control, this information should not be used as a substitution for customer's tests to ensure that SSI's products are safe, effective, and fully satisfactory for the intended end use. SSI's sole warranty is that the product will meet sales specifications in effect at the time of shipment.

STARFIRE SYSTEMS

POLYMER-TO-CERAMIC™ TECHNOLOGY

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