Development of Preceramic Polymer (polysiloxane) Precursor Materials That, When Pyrolyzed, Produce a Fire-Safe Ceramic Surface

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This presentation is derived in part from Clarke Patent WO/2009/054995, Entitled "*FIRE RESISTANT FLEXIBLE CERAMIC RESIN BLEND AND COMPOSITE PRODUCTS FORMED THEREFROM,"* April 30, 2009 (Ref. 1).

Research Objective: To develop preceramic (Ref. 2) polymer (polysiloxane) precursor materials that, when pyrolyzed, produce a fire-safe ceramic surface.

Accomplishment Description: This accomplishment was developed in three stages:
The first stage was the development of a silicone formulation that extends the elastic range of silicone composite materials from up to 300ºC (Ref. 3) to temperatures within the "red heat" zone, i.e., up to 600 to 1000ºC range (See Figure 1) of applications. The composite polymer matrix comprises a matrix of cured high, intermediate and optionally low molecular weight silicone resins including boron nitride and silica additives and reinforcing material The method for making the composite resin blend comprises mixing the silicone resins, additives with solvent, followed by stripping the solvent as the reaction mass advances forming a solvent-less resin blend for making prepreg with the reinforcement at ambient temperature without noxious odor or toxic byproducts. The prepreg was then molded and heat cured into composites that have a greater than 90% yield at 1000ºC. When the resin blend is combined with reinforcement to make composites and heat cured from 200 to 1000ºC the % recovery from 15% compression fatigue (ASTM-F-36 Rev. 95) cycle testing for 10,000,000 cycles, drops off with increasing cure temperature above 600ºC (see Figure 1).

The second stage was the development of an additional densification silicone resin for filling the porosity (Figure 2) produced when the first stage composite products' organic groups are removed by pyrolysis from test parts cured at different temperatures up to 750ºC . Consequently, there are two elastic silicone resin formulations which consist of an initial elastic preceramic matrix which becomes porous when heated to high temperatures and a second densification formulation which is used to fill the porosity at different cure temperatures which produce 20 to 40% porosity dependent upon the cure temperature of the composite. The porosity is filled efficiently by densification processing (Figure 3) in one operation utilizing a thermo-quench or by using a vacuum chamber at ambient temperature. Conversely, these same porous composites (heat cured up to 750ºC) when "densification" processed with the resin blend; unexpectedly endure the same 10,000,000 fatigue cycles with greater than 95% recovery (see Figure 4). Also, the same tensile strength was found unexpectedly to be retained up to 371ºC (700ºF) as shown in Figure 4 for three different fabric reinforced laminates after densification.

The third stage was the development of the final cure of the two silicone rubbers within the matrix, so the exterior of the high temperature polysiloxane composite readily forms a ceramic surface that will not ignite for 30 minutes at 750ºC nor produce a heat release that will contribute to the test furnace heat for at least 30 minutes. The interior silicone matrix produced by densification retains the lower elasticity revealed in Figure 1 at higher cure temperatures with laser sealed ceramic end closures. The final laminate after densification is made up of two elastic matrix polysiloxane formulations, the outer material more ceramic than the inner elastic material. When this laminate is heated in a furnace the preceramic exterior produces a ceramic barrier while the interior material retains its elastic performance capability. The interior formulation is formulateded to efficiently penetrate the porosity and to slow the rate of transformation to a ceramic from the elastic preceramic precursor. The capacity to form a protective fire safe ceramic surface which resists thermal or oxidative erosion has been demonstrated in the following tests and numerous applications.

Fire and flammability tests that have been passed by the Flexible Ceramics, Inc. materials are summarized as follows:

ASTM E 136-09 750ºC Vertical Tube Furnace Testing
Govmark Organization Inc., Farmingdale, New York.

The Flexible Ceramic densified “elastic” and preceramic polysiloxane materials are “essentially noncombustible” as evidenced by overwhelmingly passing the ASTM E-136 – 09 furnace testing (Reference 4). The test requires that specimens remain within a Vertical Tube Furnace at 750ºC (1382ºF) for at least 30 minutes, without flaming or contributing to the furnace heat. Two Flexible Ceramics, Inc. materials were tested. one an elastomeric preceramic, the other a non-elastomeric preceramic. Both materials exceeded the testing requirements and had a 98% yield.

Aircraft Advanced Fire Resistant Materials Testing
FAA fire tests (as specified by FAR 25.853); to FAA fire penetration requirements certified by National Technical Systems.
Fire blanket burn through requirements conducted by Mexmil Company in Irvine, CA.
Smoke density and heat release requirements as specified by FAR 25.853 and Boeing BSS 7239 toxicity, testing by Test Corp, Mission Viejo, CA.

Engine Combustion Durability Testing
The resin blend made into composite laminate and liquid exhaust manifold gaskets (under confidentiality agreement) has also completed over four years cab fleet (350,000 miles) and nine months truck engine dynamometer exhaust manifold (with sustained 871ºC and peak temperatures of 982ºC) durability testing with retained elastic hot gas sealing compression. The composite matrix and reinforcement forms a protective ceramic edge when laser cut at 16,500ºC. These laser cut parts have 25% higher tensile strength than when steel die cut. These composites are self extinguishing preventing pre-ignition when tested in IC engine combustion chamber ignition applications.

Significance: Prior art (Ref.5) has demonstrated within resin selection and processing the development of non-burning silicone resin composite materials, the composite material testing; however, did not include the severe 750ºC furnace test with a 98% yield. The development of two resin formulations that extend the thermal range of silicone resins also affords the use of densification to extend the elastic ceramic performance of composite structures which can readily form a fire-safe ceramic surface within severe furnace testing conditions and also when laser machined form thermally protective ceramic composite end closures. This same approach is currently being used to produce 500 to 1000ºC flexible cables, circuit boards, wire insulation, engine combustion chamber ignition devices and sensors, liquid gaskets, adhesives, coatings, sealants and honeycomb materials.

Expected Results: The produced composite laminates will readily form a fire safe ceramic surface when exposed to high heat fire conditions without ignition or contributing to the heat source. These fire-safe silicone resin composite laminates are possible candidates for the next generation aviation interior, storage, electrical and engine exhaust applications.

References:

1. Clarke, W. A., WO/2009/054995, *FIRE RESISTANT FLEXIBLE CERAMIC RESIN BLEND AND COMPOSITE PRODUCTS FORMED THEREFROM,* Publication Date: April 30, 2009

2. a. Wynne, K.J., Rice, R.W., Ann. Rev. Mater. Sci. (1984) 14, 297. b. Rice, R.W. Am Ceram. Soc. Bull. (1983) 62, 889, c. Rice, R.W. Chem. Tech. (1983) 230.

3. Sorenson, W.R. and Campbell, W. T., *Preparative Methods of Polymer Chemistry*, John Wiley & Sons (1968) p. 387.

4. ASTM International, Designation E 136-09, Standard Test Method for Behavior of Materials in a Vertical Tube Furnace at 750°C.

5. Boisvert, R. P., Burns, G. T., Chao, T. C., Katsoulis, D. E., and Kumar, S., US 5,972,512 *SILICONE RESIN COMPOSITES FOR FIRE RESISTANCE APPLICATIONS AND METHOD FOR FABRICATING SAME,* October 26, 1999.

Figures:

Figure 1

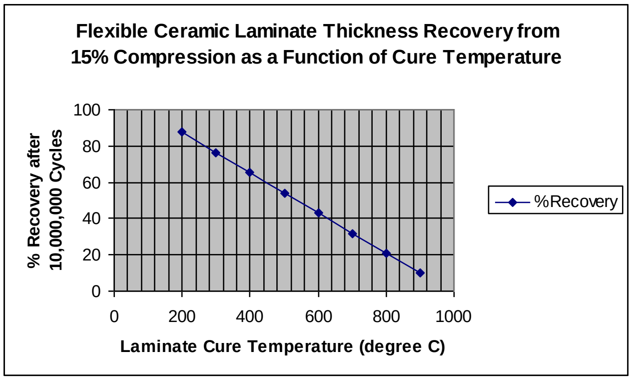


Figure 2

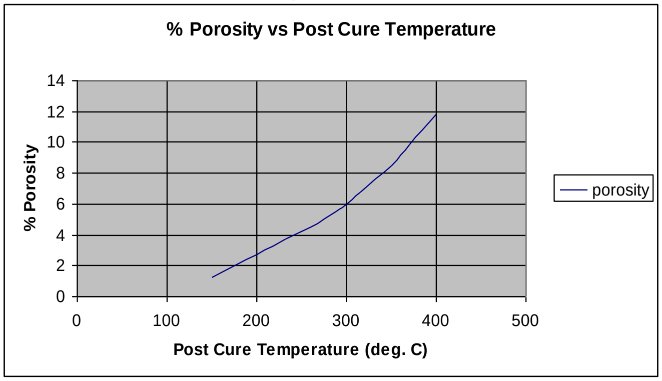


Figure 1 reveals the laminate thickness % recovery from 15% compression after 10,000,000 Fatigue cycles per ASTM-F-36 Procedure “A” for Glass fabric reinforced porous polysiloxane

Figure 3

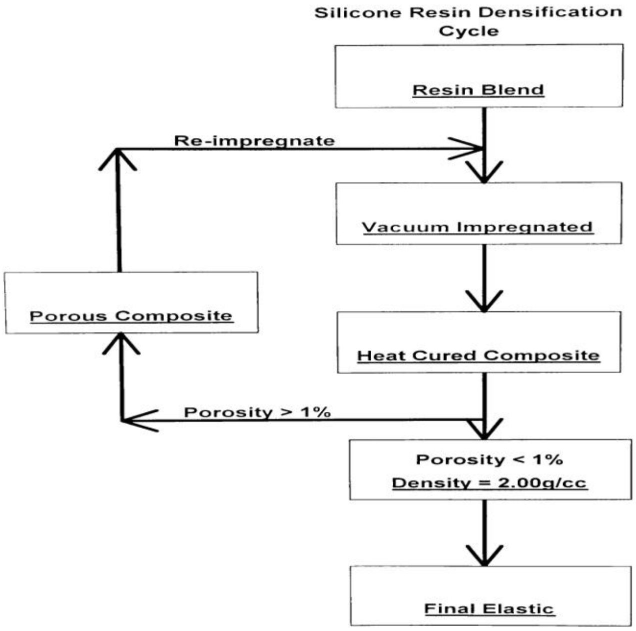
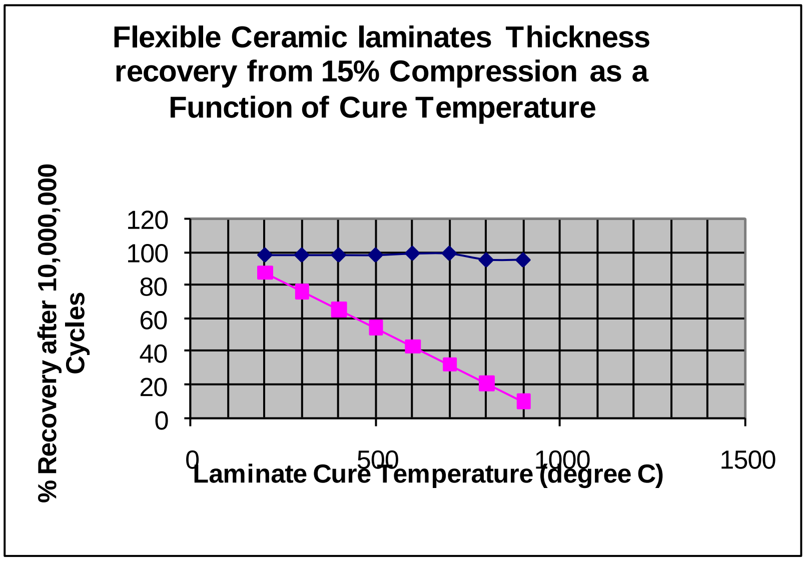


Figure 4



Top line data points represent densified recovery.
Lower line data points represent porous recovery.

TENSILE STRENGTH AND MODULUS PROPERTIES OF LAMINATE FABRIC REINFORCEMENTS AFTER DENSIFICATION ASTM D638-08

Cure Temperature (Densified after cure)		**Woven 8HS Carbon 94207 AS4-3K**		**Woven 8 HS Alumina Nextel 610-DF-11**		**Woven 8HS S-Glass S6580**	
^{o}F	(^{o}C)	Ultimate Strength (Ksi)	Modulus (Msi)	Ultimate Strength (Ksi)	Modulus (Msi)	Ultimate Strength (Ksi)	Modulus (Msi)
450	(232)	57.3	7.7	--	--	43.7	3.4
575	(302)	56.1	7.6	50.7	14.2	42.9	3.4
650	(343)	57.5	7.3	50.9	13.5		
700	(371)	58.6	7.5	50.6	14.0		