

GRAPHENE-REINFORCED CERAMIC MATRIX COMPOSITES **FROM GRAPHENE REINFORCED POLYSILAZANE**

The structure of graphite is like a ream of paper. It is a single structure composed of individual “sheets of paper”. In the case of graphite these “sheets of paper” are called graphene. In order for the graphene to be “active” and exhibit the attributes unique to graphene, the graphene sheets that make up the structure of graphite must be separated into individual sheets which are then free to incorporate into other materials such as plastics to either mechanically reinforce them or to impart unique electrical or thermal properties to them.

The problem is that in the graphite structure the graphene sheets are “glued together” by electrostatic force. However, this electrostatic force can be disrupted in several ways. Some of these methods are chemical, and some are mechanical.

The simplest way, conceptually, is to use mechanically-induced shear force. This method is analogous to simply taking a ream of paper and running your hand across the top of it. The ream of paper starts to fan out. If you continue to do this, individual stacks of paper separate out, some containing, say 50 sheets of paper, others containing, say, 30 sheets of paper. If you continue doing this, even these smaller stacks of paper separate into thinner stacks, some now containing 20 sheets of paper, and others containing only 10 sheets of paper. Continuing further, even these thinner stacks of paper separate into very thin stacks of paper, some containing 5 sheets, while others might contain only 3 sheets of paper. If you continue this process, ultimately you will only have individual sheets of paper. In the case of graphite, these individual sheets of paper are called “graphene”.

Another way to effect this process is through chemical means. Certain chemicals have the ability to “worm their way” in between the graphene “sheets of paper” in the “ream of paper” that is the graphite. In so doing, they pry the sheets of paper apart on a molecular level as they “wedge” their way between the graphene sheets. As they do this, the distance between the graphene “sheets of paper” increases. As this distance increases, the electrostatic “glue” that holds them together becomes weaker and weaker. Since the “glue” that holds the graphene sheets together has now been weakened, it becomes the individual sheets of graphene “paper” become easier to separate.

Graphene Reinforced Polysilazane is a novel, patent-pending, graphene-reinforced preceramic composition utilizing vinyl-containing polysilazane that combines both a mechanical method and a chemical method to separate graphene sheets from a graphitic structure. The utility of such a process is that polysilazane polymers do not decompose or “burn up” when you heat them, which is typical for most organic polymers. Instead, they convert to high performance engineering ceramics such as silicon carbide and silicon nitride. The net result is that the process results in a thick slurry of graphene in polysilazane that can be cast into a mold or otherwise shape-configured, solidified, and then converted to a graphene-reinforced ceramic part in a furnace. The performance benefits can be mechanical, thermal, and/or electrical. One obvious benefit is the increased fracture toughness of such graphene-reinforced ceramic matrix composites (CMC). The incorporation of graphene “sheets of paper” into the ceramic material formed by heating the polysilazane to high temperatures (pyrolysis) results in a ceramic that has high fracture toughness.

Several applications for graphene-reinforced CMCs are detailed in a paper entitled “Applications of Ceramic/Graphene Composites and Hybrids” by Cristina Marirez, Manuel Belmonte, Pilar Moranzo,

and Maria Isabel Osendi in *Materials* 2021, 14, 2071.

[https://mdpires.com/d_attachment/materials/materials-14-02071/article_deploy/materials-14-02071-v3.pdf].

Applications described include:

1. Ceramic/graphene composites for energy production and storage
2. Piezo and thermoelectric ceramic/graphene composites for energy harvesting
3. Sensors based on ceramic/graphene composites and hybrids
4. Ceramic/graphene composites for electromagnetic interference shielding
5. Catalytic applications of ceramic/graphene composites
6. Ceramic/graphene composites in biomedicine
7. Thermal applications of ceramic/graphene composites
8. Structural engineering applications of ceramic/graphene composites
9. Applications of additively-manufactured ceramic/graphene composites

Since Graphene Reinforced Polysilazane is polysilazane based, the SiCN/graphene CMC that is derived from its pyrolysis is uniquely suited to several of these applications.

The following are standard physical properties associated with Graphene Reinforced Polysilazane as provided:

Physical State: Liquid Slurry	Appearance: grey/black liquid	Density: ~0.95g/mL	Odor: Ammonia
Storage Requirements: cool, DRY and sealed	Flash Point: 61.7°F	Solvent Content: NA	Solids %: 20 (wt)

The following process descriptions are provided to assist in the manufacture of a SiCN/graphene CMC from Graphene Reinforced Polysilazane:

Graphene Reinforced Polysilazane is weighed into a 35mL glass test tube ~30g. Next, about 0.05g of Fe(II)AcAc and about 5g of 80% Luperox 531M80 are added to the test tube and mixed thoroughly through aspiration. Allow the material to cure for ~5 days at R.T., or warm the material in a water bath heated to ~45°C overnight. Material that is heated at ~45°C overnight has a lower odor and higher integrity than the material that is allowed to cure at ambient temperature.

Cured GeraGraphe GC can then be placed in ceramic racks held horizontally in a furnace equipped with an Argon gas inlet and a programmable temperature module. The material is subjected to the following pyrolysis ramp with ~5CFM of Argon flow into the furnace during the entire program.

Program	Ramp, °C/min	Hold temp, °C	hold Time
	10	450	4 hrs
	10	750	4 hrs
	10	1200	4 hrs

Sample	Weight Prior to pyrolysis	Weight post pyrolysis
Graphene Reinforced Polysilazane	42.1g	36.4g
	Volume prior to pyrolysis	Volume post pyrolysis
	35 cm ³	19.2 cm ³
	Density Prior to pyrolysis	Density post pyrolysis
	1.2 g/cm ³	1.90 g/cm ³

Figure 1 is a photograph that shows a cylindrical, unpyrolyzed sample of a fully cured vinyl-containing polysilazane prepared by curing the liquid polysilazane in a test tube and a similar, cylindrical sample of a fully cured cylinder of Graphene Reinforced Polysilazane that was subjected to the pyrolysis ramp described above. The shrinkage of the part from its original “test tube” derived dimensions and its corresponding increase in density to that of a ceramic material can be observed in the photograph.



FIGURE 1

A SiCN/graphene CMC containing a ceramic particulate phase can also be prepared. For instance, when 12.5 wt% of 10 micron SiC powder is added to Graphene Reinforced Polysilazane, and that mixture is processed as below using the same setup and pyrolysis atmosphere as above, a CMC having the following properties is obtained:

Program	Ramp, °C/min	Hold temp F	hold Time
---------	--------------	-------------	-----------

	10	450	4 hrs
	10	750	4 hrs
	10	1200	4 hrs

The following table shows weights, dimensions and densities that are obtained both pre- and post-pyrolysis showing densities characteristic of the Graphene Reinforced Polysilazane-derived CMC.

Sample	Weight Prior to pyrolysis	Weight post pyrolysis
Graphene Reinforced Polysilazane + 12.5 wt% SiC	49.1g	42.4g
	Volume Prior to Pyrolysis	Volume post pyrolysis
	35 cm ³	18.9 cm ³
	Density Prior to pyrolysis	Density post pyrolysis
	1.4g/cm ³	2.2g/cm ³

Figure 2 is a photograph that shows a cross section of the dense, non-porous ceramic formed by pyrolyzing a fully cured sample of Graphene Reinforced Polysilazane further containing 12.5% of 10 micron SiC particulate.



FIGURE 2

In summary, Graphene Reinforced Polysilazane provides a convenient route to preparing SiCN/graphene composites useful for a variety of high performance applications. It is provided as a

relatively low viscosity liquid dispersion that can be molded or infiltrated into porous preforms, shape-stabilized at either ambient temperature or above through the addition of a metal/peroxid catalyst combination, and then pyrolyzed to the desired ceramic/graphene composition.

Graphene Reinforced Polysilazane is available from Agostyx LLC, and is patent-pending under U.S. Provisional Patent Application No. 63/211,545 entitled "Polymer-Derived, Graphene Reinforced Ceramic Matrix Composites", filed June 16, 2021.

Graphene Reinforced Polysilazane can be purchase by contacting
at.....