

Serial No. 775,486  
Filing Date 31 December 1996  
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3                   OXIDATION RESISTANT FIBER-REINFORCED COMPOSITES WITH  
4                   POLY(CARBORANE-SILOXANE/SILANE-ACETYLENE)  
5

6                                   **Background of the Invention**

7           **Field of the Invention**

8                   The invention relates to fiber-reinforced composites and, more specifically, to composites  
9           having fibers dispersed through a thermoset or ceramic matrix wherein the matrix is formed by  
10           curing or pyrolyzing a linear polymer having repeating units of carborane, siloxane or silane and  
11           acetylene.

12           **Background of the Related Art**

13                   Fiber-reinforced composites, for example, carbon-carbon composites having carbon fibers  
14           embedded in a carbonaceous matrix, are strong, lightweight materials that have many uses,  
15           including as structural components in missile, aircraft and aerospace vehicles.

16                   A drawback to using fiber-reinforced composites in harsh environments is that the matrix  
17           or the fibers may oxidize and erode when exposed to high temperatures, causing a breakdown  
18           and failure of the composite material. Efforts have been made to improve the oxidation resistance  
19           of fiber-reinforced composites by creating a barrier coating over the material or by adding  
20           compounds containing boron and silicon or other refractory elements to the fibers or the matrix.  
21           For example, U.S. Pat No. 4,668,579 to Strangman *et al* describes a carbon-carbon fiber

1 composite that is protected from oxidation by having a protective underlayer of boron carbide and  
2 a protective overlayer of silicon carbide deposited onto the fibers by chemical vapor deposition  
3 (CVD). Under oxidating conditions, the boron carbide and silicon carbide are converted into  
4 boron oxide and silicon dioxide. U.S. Pat No. 4,894,286 to Gray describes an oxidation-resistant  
5 carbonous composite having boron, silicon and titanium elements or compounds dispersed  
6 throughout the structure. The boron, silicon and titanium are added in the form of powders to the  
7 precursor resin that becomes the carbonous matrix. When the composite is exposed to high  
8 temperatures in an oxidizing environment, the boron, silicon and titanium serve as oxygen getters  
9 to protect the composite from oxidation. The boron, silicon and titanium are converted into oxides  
10 to form a sealant glass that fills microcracks in the composite. In each of the above composites,  
11 the effectiveness of the thermal protection depends on how well or how thoroughly the protective  
12 elements can be dispersed throughout or coated onto the composite.

13 It is an object of the invention to provide an oxidation resistant fiber-reinforced composite  
14 that has protective components coated onto the fibers and homogeneously distributed throughout  
15 the composite. It is a further object of the invention to provide an oxidation resistant fiber-  
16 reinforced composite made from materials that are easily processed.

17 It has recently been discovered that boron-containing, silicon-containing and carbon-  
18 containing moieties can be combined into linear inorganic-organic hybrid polymers that can be  
19 used to make oxidatively stable thermosets and ceramics. Such linear inorganic-organic hybrid  
20 polymers, specifically, carborane-siloxane/silane-acetylene polymers and their corresponding  
21 thermosets and ceramics, are disclosed in U.S. Pat. No. 5,272,237; 5,292,779; 5,348,917 and

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1 5,483,017, in the U.S. Patent Application entitled "Thermoset Polymers Made by Blending  
2 Poly(carborane-siloxane/silane-acetylene) and Poly(siloxane-acetylene)" filed November 13, 1996,  
3 and in the U.S. Patent Application entitled "Improved Method for Synthesis of Linear Inorganic-  
4 Organic Hybrid Polymers" filed as a Statutory Invention Registration on November 27, 1996.  
5 Polymers that include carboranyl, silyl or siloxyl and acetylenic groups in the same polymeric  
6 chain combine the desirable features of both inorganics and organics: the carborane groups  
7 provide thermal and oxidative stability, the silane or siloxane groups provide additional thermal  
8 stability and chain flexibility and the acetylenic groups allow cross-linking of adjacent polymer  
9 strands to form thermosets. Carborane-silane/siloxane-acetylene polymers have the advantage of  
10 being extremely easy to process and convert into thermosets or ceramics since they are either  
11 liquids at room temperature or low melting solids and are soluble in most organic solvents.

### 13 Summary of the Invention

14 It has now been found that poly(carborane-siloxane/silane-acetylene) thermosets and  
15 ceramics can be used to create oxidation resistant fiber-reinforced composites and that cured or  
16 pyrolyzed carborane-siloxane/silane-acetylene polymers protect the fibrous material in a fiber-  
17 reinforced composite from oxidation at elevated temperatures. An oxidation resistant fiber-  
18 reinforced composite according to the present invention is formed by impregnating a fibrous  
19 material with a resin comprising a linear polymer having a repeating unit comprising at least one  
20 carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group. The linear  
21 polymer is then cured to form a fiber-reinforced thermoset or pyrolyzed to form a fiber-reinforced

1 ceramic. For additional protection, the fibrous material may be prewetted or coated, also with a  
2 linear polymer having a repeating unit comprising at least one carboranyl group, at least one silyl  
3 or siloxyl group and at least one acetylenic group, prior to being impregnated. The coating on  
4 the fibrous material may be cured to form a thermoset coating on the fibers or may be pyrolyzed  
5 to form a ceramic coating on the fibers.

6 Using a linear polymer that has silicon-containing and boron-containing moieties  
7 incorporated directly into the backbone of the polymer chain to coat the fibrous material and to  
8 form the matrix of the composite ensures that the silicon-containing and boron-containing  
9 moieties are spread homogeneously onto the fibers and throughout the composite and ensures that  
10 no gaps or microcracks occur that could lead to thermal failure of the composite. Because  
11 carborane-silane/siloxane-acetylene polymers are generally liquid at room temperature, the  
12 polymers are easy to process and easy to use for coating and impregnating a fibrous material.

### 13 **Detailed Description of the Preferred Embodiments**

14 The following detailed description of the invention is provided to aid those skilled in the  
15 art in practicing the present invention. However, the following detailed description of the  
16 invention should not be construed to unduly limit the present invention. Variations and  
17 modifications in the embodiments discussed may be made by those of ordinary skill in the art  
18 without departing from the scope of the present inventive discovery.

19 The invention relates to an oxidation resistant composite made up of a thermoset or  
20 ceramic matrix and reinforcing fibers dispersed within the matrix. The matrix is a product  
21 obtained by curing or pyrolyzing a linear polymer having a repeating unit comprising at least one

1 carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group.

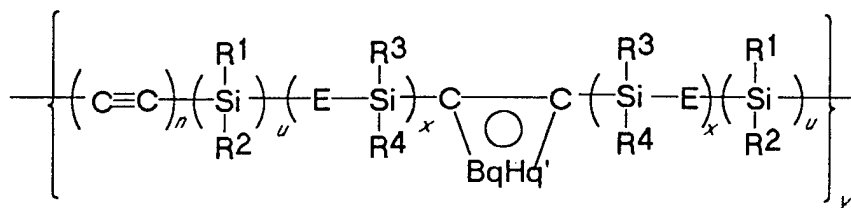
2           The invention further relates to oxidation resistant fiber/thermoset and fiber/ceramic  
3 composites and methods of making them by the process of applying a first linear polymer having  
4 a repeating unit comprising at least one carboranyl group, at least one silyl or siloxyl group, and  
5 at least one acetylenic group, to a fibrous material to create a coating of the first linear polymer  
6 on the fibrous material, impregnating the coated fibrous material with a resin that includes a  
7 second linear polymer having a repeating unit comprising at least one carboranyl group, at least  
8 one silyl or siloxyl group, and at least one acetylenic group and either curing the impregnated  
9 fibrous material to create a fiber/thermoset composite or pyrolyzing the impregnated fibrous  
10 material to create a fiber/ceramic composite.

11           The fibrous material used in the present invention can be any two-dimensional or three-  
12 dimensional, woven or nonwoven fibrous material useful in creating fiber-reinforced composites.  
13 Examples of useful fibers and fibrous materials are given in U.S. Pat No. 4,894,286 and U.S. Pat.  
14 No. 5,002,750, the entire disclosures of which are hereby incorporated herein by reference.  
15 Preferably, the fibers are carbon fibers or silicon carbide fibers. The terms "fibers" and "fibrous  
16 material" are used interchangeably herein to refer to any type of reinforcing fiber.

17           The first linear polymer, used to coat the fibrous material before it is impregnated, and  
18 the second linear polymer, used to impregnate the fibrous material and which becomes the matrix  
19 of the fiber-reinforced composite, are linear carborane-silane/siloxane-acetylene polymers such  
20 as are described in U.S. Pat. No. 5,272,237, U.S. Pat No. 5,292,779, U.S. Pat No. 5,348,917,  
21 U.S. Pat. No. 5,483,017, the U.S. Patent Application entitled "Thermoset Polymers Made by

Inventor's Name: Teddy M. Keller and David Y. Son

1 Blending Poly(carborane-siloxane/silane-acetylene) and Poly(siloxane-acetylene)" filed November  
 2 13, 1996, and the U.S. Patent Application entitled "Improved Method for Synthesis of Linear  
 3 Inorganic-Organic Hybrid Polymers" filed as a Statutory Invention Registration on November 27,  
 4 1996. The disclosures of the above patents and patent applications are hereby incorporated by  
 5 reference. The first linear polymer and the second linear polymer are preferably compounds  
 6 selected from the group consisting of



(1)

8  
 9 wherein:

10 (1)  $n$  is an integer from 1 to 12 and  $u$  and  $y$  are positive integers;

11 (2)  $\left( \text{C}\equiv\text{C} \right)_n$  represents an unconjugated acetylenic group or conjugated  
 12 acetylenic groups when  $n$  is an integer greater than 1;

13  
 14 (3)  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  may be the same or different and are selected from the group  
 15 consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof;

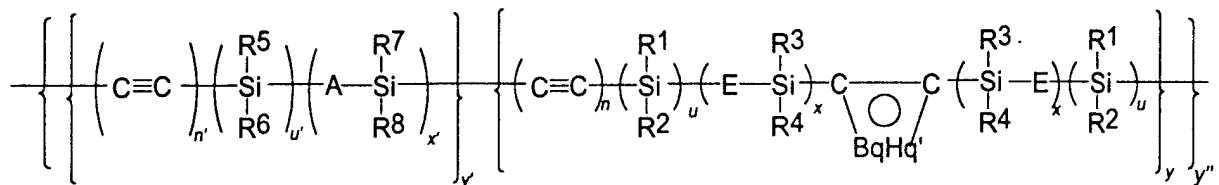
16 (4)  $\begin{array}{c} \text{C} \text{---} \text{C} \\ \diagdown \quad \diagup \\ \text{O} \\ \diagup \quad \diagdown \\ \text{BqHq}' \end{array}$  represents a carboranyl group; and

17 (5)  $q$  and  $q'$  are integers from 3 to 16;

18  
 19 (6)  $x$  represents an integer greater than or equal to zero; and

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- (7) E is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof; and



(3)

wherein

- (1)  $n$  and  $n'$  are integers from 1 to 12 and  $u$ ,  $u'$ ,  $y$ ,  $y'$  and  $y''$  are positive integers;

- (2)  $\left( \text{C}\equiv\text{C} \right)_n$  and  $\left( \text{C}\equiv\text{C} \right)_{n'}$  represent unconjugated acetylenic groups or

conjugated acetylenic groups when  $n$  and  $n'$  are integers greater than 1;

- (3)  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  may be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof;

- (4)  $\begin{array}{c} \text{---C---C---} \\ \diagdown \quad \diagup \\ \text{O} \\ \text{BqHq}' \end{array}$  represents a carboranyl group; and

- (5)  $q$  and  $q'$  are integers from 3 to 16;

- (6)  $x$  and  $x'$  represent integers greater than or equal to zero; and

- (7) E is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof;

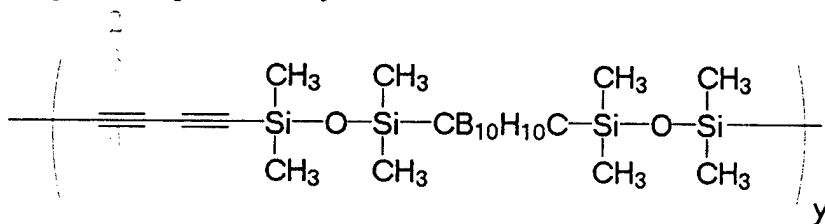
- (8) A is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof



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1           (9)    wherein A and E may be the same or different;

2           The first linear polymer and the second linear polymer may be the same or different, but are  
3           preferably the same. Most preferably, the first linear polymer and the second linear polymers are  
4           compounds represented by the formula:

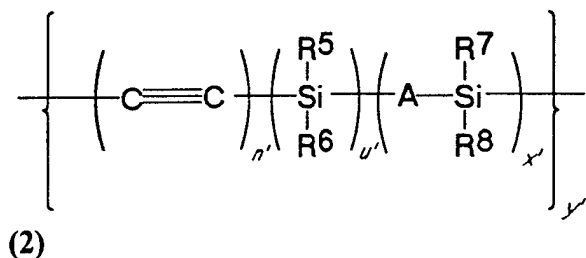


6           (1')

7           where y is a positive integer.

8           To reduce costs, it may sometimes be desirable to reduce the amount of carborane in the  
9           fiber-reinforced composite, relative to the amount of silane or siloxane and acetylene. This can  
10          be done by using first linear polymers and second linear polymers that have a lesser amount of  
11          carborane relative to other substituents. An example of such a linear polymer is that represented  
12          by formula (3) above (and described in U. S. Patent No. 5,483,017) wherein y' is greater than y  
13          (that is, where the number of silane/siloxane-acetylene units is greater than the number of  
14          carborane units), or by adding to the coating for the fibrous material and to the resin for  
15          impregnating the fibrous material a linear non-carborane-containing polymer represented by the  
16          formula:

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12

wherein:

(1)  $n'$  is an integer from 1 to 12 and  $u'$  and  $y'$  are positive integers;

(2)  $\left( \text{C} \equiv \text{C} \right)_{n'}$  represents an unconjugated acetylenic group or conjugated

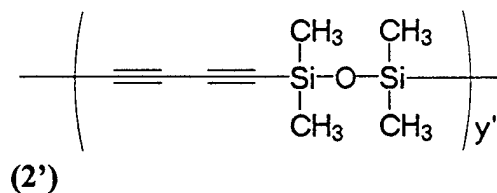
acetylenic groups when  $n$  is an integer greater than 1.

(3)  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$  may be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof;

(4)  $x'$  represents an integer greater than or equal to zero; and

(5) A is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof.

13 The linear non-carborane-containing polymer is preferably a compound of the formula



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16  
17

where  $y'$  is an integer. Examples of mixtures of carborane-containing and non-carborane-containing linear polymers are described in the U.S. Patent Application entitled "Thermoset

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1 Polymers Made by Blending Poly(carborane-siloxane/silane-acetylene) and Poly(siloxane-  
2 acetylene)" filed by the present inventors on November 13, 1996. These mixtures can be used to  
3 coat and impregnate the fibrous material to create fiber-reinforced thermoset and ceramic  
4 composites with a reduced amount of carborane.

5 Although fibrous material may be impregnated directly with the resin that includes the  
6 second linear polymer to form a fiber-reinforced composite according to the present invention  
7 without going through a prewetting or coating step, it is preferred that the fibers be prewetted or  
8 coated with the first linear polymer before the impregnation step. Prewetting or coating the  
9 fibrous material with the first linear polymer may be accomplished by any method known in the  
10 art and is preferably done by diluting the first linear polymer with a suitable solvent such as  
11 methylene chloride, dipping the fibrous material into the dilute solution and then air-drying the  
12 fibrous material to remove the solvent and leave a coating of the first linear polymer on the  
13 fibrous material. When the fibrous material is composed of fibers such as carbon fibers that are  
14 particularly prone to oxidation, it is preferable that the first linear polymer be coated onto the  
15 fibrous material and then be cured or pyrolyzed to create a thermoset coating or a ceramic coating  
16 on the fibers. Curing of the first linear polymer to create a thermoset coating is carried out by  
17 exposing the coated fibrous material to heat, typically at a temperature above about 150° C and  
18 below about 450° C or to light to effect the cross-linking of the carbon-carbon triple bonds of  
19 the acetylene moieties of the polymer. The preferred temperature for curing by heating is below  
20 450° C, since pyrolysis begins to occur above that temperature. If light is used to effect the cross-  
21 linking, the preferred wavelength is in the uv range. Pyrolysis of the first linear polymer to create

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1 a ceramic coating is carried out by exposing the coated fibrous material to sufficient heat,  
2 generally above about 450° C, to convert the polymer into a ceramic. For even greater protection  
3 against oxidation, the steps of coating and curing or of coating and pyrolyzing may be repeated  
4 to create layers of the thermoset coating or the ceramic coatings on the fibers.

5 The step of impregnating the fibrous material with the resin that includes the second linear  
6 polymer may be carried out by any method known in the art for creating a fiber-reinforced  
7 composite, including by adding the resin to the fibrous material or by adding the fibrous material  
8 to the resin. Preferably, the resin is composed primarily of the second linear polymer or of a  
9 mixture of the second linear polymer and a non-carborane-containing linear polymer as described  
10 above. Curing of the impregnated fibrous material to create a fiber/thermoset composite is carried  
11 out by exposing the impregnated fibrous material to heat, typically above about 150° C and below  
12 about 450° C, to effect the cross-linking of the carbon-carbon triple bonds of the second linear  
13 polymer. Exposing the fibrous material to heat in this temperature range would also effect curing  
14 of any previously uncured first linear polymer attached to the fibers. Pyrolysis of the impregnated  
15 fibrous material to create a fiber/ceramic composite is carried out by exposing the impregnated  
16 fibrous material to sufficient heat, typically above about 450° C, preferably above about 700° C  
17 to convert the second linear polymer into a ceramic. Exposing the fibrous material to heat above  
18 about 450° C would also effect pyrolysis of any previously unpyrolyzed first linear polymer  
19 attached to the fibers.

20 In making ceramic-coated fibers or fiber-reinforced ceramics, it is important to avoid  
21 creating defects or disruptions that may be caused by the evolution of volatiles during the

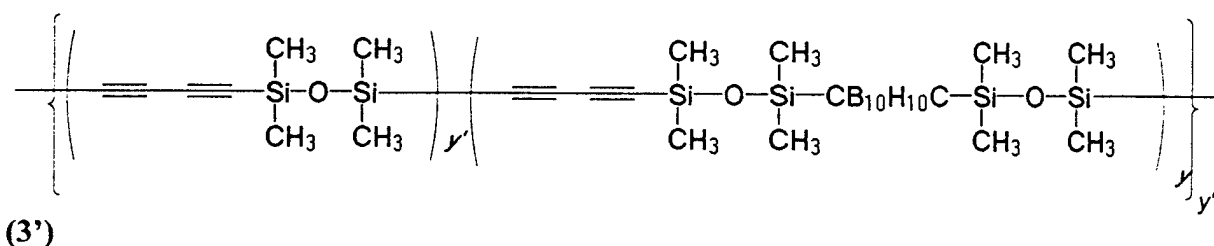
1 pyrolyzing process. Such an evolution of volatiles can be caused by heating a pyrolyzable  
2 material too rapidly in the temperature range where volatiles are most likely to be produced,  
3 generally in the range between about 500° C and about 700° C. In making ceramic-coated fibers  
4 or fiber/ceramic composites according to the present invention, the damage to the coating on the  
5 fibers from the evolution of volatiles during the pyrolyzing process can be minimized by limiting  
6 the heating rate of the coated fibers or the impregnated fibrous material in the range between  
7 about 500° C and about 700° C to less than about 1° C per minute.

8 Pyrolysis of the coated fibrous material or the impregnated fibrous material by heating to  
9 a temperature above about 450° C necessarily proceeds through an intermediate step of curing  
10 the first linear polymer or the second linear polymer, since to reach the pyrolysis temperature,  
11 the material must be brought through the temperature range that effects curing. In some instances,  
12 it may be desirable to cure the coated fibrous material or the impregnated fibrous material and  
13 then carry out pyrolysis at a subsequent time. Accordingly, the invention includes a fiber/ceramic  
14 composite made by the process of applying a coating of the first linear polymer to the surfaces  
15 of a fibrous material curing the first linear polymer to create a thermoset coating on the fibrous  
16 material, pyrolyzing the thermoset coated fibrous material to create a ceramic coating on the  
17 fibrous material, impregnating the ceramic coated fibrous material with the resin that includes the  
18 second linear polymer, curing the impregnated fibrous material to create a fiber/thermoset  
19 composite, and then pyrolyzing the fiber/thermoset composite to create a fiber/ceramic composite.

### 21 Examples

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The following examples outline preferred embodiments of the present invention. In the examples, the term poly(carborane-siloxane-acetylene) refers to a polymer represented by formula (1'), above. The term poly(carborane-siloxane-acetylene) copolymer refers to a compound represented by the formula:



wherein  $y$ ,  $y'$  and  $y''$  are integers and wherein the ratio of  $y'$  to  $y$  is 9:1.

#### Example 1. Oxidation of Carbon Fibers. (comparative example)

Carbon fibers were weighed onto a TGA platinum pan and dried by heating to 200°C under inert conditions. Heat treatment of the fibers to 1000°C under a flow of air resulted in a catastrophic decomposition of the fibers between 600 and 800°C. At 800°C, the carbon fibers had been completely consumed.

#### Example 2. Coating of Carbon Fibers with Poly(carborane-siloxane-acetylene).

A sample (0.06 g) of poly(carborane-siloxane-acetylene) was weighed into a 30 ml beaker. Methylene chloride (0.5 ml) was added with stirring to dissolve the polymer. Chopped carbon fibers were then dipped into the solution and air dried initially. The coated fibers were irradiated by uv light for 5 hours in an attempt to obtain some cross-linking involving the acetylenic

1 linkages. A sample of the coated fibers were then placed in a TGA platinum pan and a  
2 thermogram was obtained to 1000° C. During the heat treatment at 10° C/min, the sample lost  
3 approximately 15 % weight. Upon cooling, the ceramic coated carbon fibers was reheated in the  
4 TGA chamber to 1000° C under a flow of air (50 cc/min). The sample was completely stable to  
5 600° C. Between 600 and 800° C, the ceramic coated carbon fibers lost about 27 % weight. From  
6 800 to 1000° C, no further weight loss was observed. The observed weight loss may be due to  
7 microcracking that occurred during the heat treatment and formation of the ceramic coating on  
8 the carbon fibers. Such microcracking would allow some oxidation to occur before the boron can  
9 oxidize and seal the cracks resulting in a cessation of oxidation of the carbon. Upon cooling back  
10 to room temperature, the sample was rescanned several time under a flow of air to 1000° C. No  
11 further changes were observed. The sample was then aged in a flow of air at 400, 500, 600, 700,  
12 800, and 900° C for 5 hours at each temperature resulting in no weight loss but an increase in  
13 weight of about 0.7 % was observed.

14  
15 **Example 3. Multiple Ceramic Coatings on Carbon Fibers to Protect Against Oxidation.**

16  
17 Carbon fibers were dipped into a dilute methylene chloride solution of poly (carborane-siloxane-  
18 acetylene). After air drying, the fiber were placed into an oven preheated to 300° C and heated  
19 for 30 minutes to convert the film of poly (carborane-siloxane-acetylene) to a thermoset. The  
20 coated fibers were then placed into a TGA platinum pan and heated at 10° C/min to 1000° C in  
21 a flow of nitrogen. Upon cooling, the ceramic coated fibers were removed from the pan and

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1 dipped into the solution of poly (carborane-siloxane-acetylene) prepared above. After air drying,  
2 the fiber were placed into an oven preheated to 300° C and heated for 30 minutes to convert the  
3 film of poly (carborane-siloxane-acetylene) to a thermoset. The second layer coated fibers were  
4 then placed into a TGA platinum pan and heated at 10° C/min to 1000° C in a flow of nitrogen.  
5 Upon cooling the ceramic coated fibers were removed from the pan and again dipped into the  
6 solution of poly (carborane-siloxane-acetylene) prepared above. After air drying, the fibers were  
7 placed into an oven preheated to 300° C and heated for 30 minutes to convert the film of poly  
8 (carborane-siloxane-acetylene) to a thermoset. The third layer coated fibers were then placed into  
9 a TGA platinum pan and heated at 10° C/min to 1000° C in a flow of nitrogen. Upon cooling to  
10 room temperature, the carbon fibers coated with three layers of ceramic material were heated at  
11 10° C/min to 1000° C under a flow of air (50 cc/min). The coated fibers did not lose any weight  
12 until above 600° C. Between 600 and 800° C, the coated fiber composition lost about 49 %  
13 weight. No further weight loss was observed upon heat treatment to 1000° C.

14  
15 **Example 4. Formation of Oxidatively stable Carbon Fiber/Ceramic Composite By Slow Heat**  
16 **Treatment.**

17  
18 Carbon fibers were dipped into a dilute methylene chloride solution of poly (carborane-siloxane-  
19 acetylene). After air drying, the fiber were placed into an oven preheated to 300° C and heated  
20 for 1 hour to convert the film of poly (carborane-siloxane-acetylene) to a thermoset. The coated  
21 fibers were then placed into a TGA platinum pan. Poly (carborane-siloxane-acetylene) was then



1 added to the pan to cover the fibers. The fiber/poly (carborane-siloxane-acetylene) composition  
2 was then slowly heated at 1° C/min to 1000° C in a flow of nitrogen. At 1000° C the carbon  
3 fiber/ceramic composite exhibited a char yield of about 87 %. Upon cooling back to room  
4 temperature, the composite was heated in a flow of air (50 cc/min) at 1° C/min to 1000° C. From  
5 100 to about 515° C, the composite gained about 0.2% weight. From 515 to about 680° C, the  
6 composite lost about 3.5% weight. Between 680 and 920° C, an additional 0.5% weight was lost.  
7 Between 920 and 1000° C, some weight gain was observed.  
8

9 **Example 5. Oxidative Aging Studies on Carbon Fiber/Ceramic Composite.**

10  
11 The carbon fiber/ceramic composite from Example 4 was further aged in a flow of air (50  
12 cc/min) at 400, 500, 600, and 700° C for 5 hours at each temperature. The ramp rate was 10  
13 °C/min. During the heat treatment at 400° C, the composite sample gained about 0.4% weight.  
14 Very little weight changes occurred for the additional heat treatments at 500, 600, and 700° C.  
15 Examples 4 and 5 demonstrate that it is possible to protect carbon fibers against oxidation by  
16 slowly increasing the temperature during the preparation of the thermoset based composite and  
17 conversion to a carbon fiber/ceramic composite.  
18

19 **Example 6. Fabrication of Carbon Reinforced Composite Using Woven Carbon Fabric (T-**  
20 **650, 5K) and poly (carborane-siloxane-acetylene) copolymer (10/90) by Resin Infusion**  
21 **Molding.**

1 A dam (6"x6") was built on an aluminum plate by using a high temperature sealant tape on top  
2 of 1/4" rods. Poly (carborane-siloxane-acetylene) copolymer (8.12 g) was placed evenly inside  
3 of the dam. Six layers of woven carbon fabric (T-650, 5K) were placed on top of the copolymer.  
4 A peel ply, porous bleeders, and a caul plate made of aluminum was then placed on top of the  
5 carbon fabric. The aluminum plate assembly was vacuum sealed inside of kapton film. A vacuum  
6 was then pulled on the system while heating. At 100° C, it was observed that the copolymer had  
7 soaked through the carbon fabric into the bleader. The fabrication of the composite was achieved  
8 by the following cure cycle: 200° C for 1.5 hours, 250° C for 1.5 hours, and 300° C for 1 hours.

9  
10 **Example 7. Oxidative Studies on Silicon Carbide Fibers.** (comparative example)

11  
12 Chopped silicon carbide (SiC) fibers were weighed into a TGA platinum pan and dried by heating  
13 at 300° C for 30 minutes under a nitrogen atmosphere. Upon cooling the fibers were heated at 10°  
14 C/min under a flow of air (50 cc/min) to 1000° C. No weight loss occurred during the heat  
15 treatment. Moreover, about 1.2% weight gain was observed due apparently to some surface  
16 oxidation.

17  
18 **Example 8. Formation of Silicon Carbide/Ceramic Composite by Slow Heat Treatment of**  
19 **Silicon Carbide/Poly (Carborane-Siloxane-Acetylene) Composition.**

20  
21 Silicon Carbide fibers were dipped into a dilute methylene chloride solution of poly (carborane-

1 siloxane-acetylene). After air drying, the coated fibers were placed into a TGA platinum pan.  
2 Poly (carborane-siloxane-acetylene) was then added to the pan to cover the fibers. The fiber/poly  
3 (carborane-siloxane-acetylene) composition was then slowly heated at 1° C/min to 1000° C in a  
4 flow of nitrogen. At 1000° C, the carbon fiber/ceramic composite exhibited a char yield of about  
5 88 %. Upon cooling back to room temperature, the composite was heated in a flow of air (50  
6 cc/min) at 1° C/min to 1000° C. From 100 to 1000° C, the composite gained about 0.75% weight.

7  
8 **Example 9. Formation of Silicon Carbide/Ceramic Composite by Slow Heat Treatment of**  
9 **Silicon Carbide/Poly (Carborane-Siloxane-Acetylene) Copolymer Composition.**

10  
11 Silicon Carbide fibers were dipped into a dilute methylene chloride solution of poly (carborane-  
12 siloxane-acetylene) copolymer containing 10 molar percent of carborane. After air drying, the  
13 coated fibers were placed into a TGA platinum pan. Poly (carborane-siloxane-acetylene)  
14 copolymer was then added to the pan to cover the fibers. The fiber/poly (carborane-siloxane-  
15 acetylene) copolymer composition was then slowly heated at 1° C/min to 1000° C in a flow of  
16 nitrogen. At 1000° C, the carbon fiber/ceramic composite exhibited a char yield of about 87 %.  
17 Upon cooling back to room temperature, the composite was heated in a flow of air (50 cc/min)  
18 at 1° C/min to 1000° C. From 100 to 1000° C, the composite gained about 0.85% weight.

19 Obviously, many modifications and variations of the present invention are possible in light  
20 of the above teachings. It is therefore to be understood that

21 the invention may be practiced otherwise than as specifically described.

Docket No.: N.C. 77105  
Inventor's Name: Teddy M. Keller and David Y. Son

PATENT APPLICATION

### ABSTRACT

An oxidation resistant fiber-reinforced composite is made by impregnating a fibrous material with a resin containing a linear polymer having a repeating unit with at least one carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group. The linear polymer may then be cured to form a fiber-reinforced thermoset or may be pyrolyzed to form a fiber-reinforced ceramic. For additional protection of the fibrous material against oxidation, the fibrous material may be prewetted or coated, also with a linear polymer containing a linear polymer having a repeating unit with at least one carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group, prior to being impregnated. The coating on the fibrous material may be cured to form a thermoset coating on the fibers or may be pyrolyzed to form a ceramic coating on the fibers.