COPOLYMER SEALANT COMPOSITIONS
AND METHOD FOR MAKING

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Field of Search

References Cited

Abstract
Condensation curable poly(fluoroorgano)siloxane-poly(silarylene)siloxane block copolymer compositions having a glass transition temperature not exceeding about –54°C and excellent solvent resistance have been found useful as sealants. Polyalkoxysilylorgano compounds, such as 1,4-bis[trimethoxysilyl(ethyl)]benzene have been found to be effective as cross-linkers.

25 Claims, No Drawings
COPOLYMER SEALANT COMPOSITIONS AND METHOD FOR MAKING

This application is a divisional of application Ser. No. 09/626,768, filed Jul. 27, 2000, which is hereby incorporated by reference in its entirety, now U.S. Pat. No. 6,451,954.

The present invention is based on work sponsored under NASA’s High Speed Research Contract NASI 20220, with Boeing under subcontract ZA0073 Task 22, Subtask 4.2.2.4.

BACKGROUND OF THE INVENTION

The present invention is directed to copolymer compositions useful in the preparation of fuel tank sealants. More particularly, the present invention relates to condensation curable poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer compositions and the use of polyalkoxysilylorganic compounds as cross-linkers to facilitate the condensation cure of poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymers.

As shown by Smith, U.S. Pat. No. 3,109,826, bis (alkoxysilyl) hydrocarbons, such as 1,2-bis(triethoxysilyl)ethane, can be used as cross-linkers in combination with a metal salt to effect the neutral condensation cure of hydroxy end-blocked polydiorganosiloxanes. However, the resulting cured silicone compositions have been found to be problematic as aircraft fuel tank sealants, as they do not have the required solvent or fuel resistance. It is known that fluoroorganosilicones, for example, made by polymerizing tris [trifluoropropyl)methyl]cyclosiloxane, can provide excellent fuel resistance. However, fluoroorganosilicones often do not meet the wide temperature stability requirements needed in aircraft sealants, such as temperatures in a range between -54°C and 177°C over an extended period of time. In addition, fluoroorganosilicones are subject to depolymerization which can result in the formation of low molecular weight cyclics.

In an effort to enhance the thermal stability of fluoroorganosilicones, non-siloxane groups, such as p-silphenylene, have been inserted into the polyfluorosiloxane backbone, as shown by Grassie and Beattie, “The Thermal Degradation of Polysiloxanes: Part 7”, Polymer Degradation and Stabilization 8:177-193 (1984). It is also reported by Dvornic and Lenz, Macromolecules, 25, 3769 (1992), that copolymers having a glass transition temperature (Tg) of -51°C can be made by reacting methyl(3,3,3-trifluoropropyl)methyl)cyclosiloxane. However, fluoroorganosilicones often do not meet the wide temperature stability requirements needed in aircraft sealants, such as temperatures in a range between -54°C and 177°C over an extended period of time.

Experience also has shown that in addition to being sensitive to depolymerization, condensation curable fluorosilicone compositions often suffer from an incomplete cure using a conventional curing catalyst, such as a tin salt, and a standard neutral condensation curable cross-linker, for example a polyalkoxysiloxane. One possible explanation, as discussed by Fujiki, U.S. Pat. No. 5,236,997, is that the steric hindrance or electronic effects of bulky terminal trifluoropropyl groups inhibit crosslinking of the network.

Accordingly, depolymerization resistant silicone base copolymers which could be compounded to a fuel resistant condensation curable silicone composition convertible to the elastomeric state upon cure exhibiting stability over an operable temperature in a range between about -54°C or below and at least about 177°C over an extended period of time are constantly being sought which also exhibit low temperature flexibility, in addition to high temperature stability.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a condensation curable poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about -54°C.

In yet a further embodiment of the present invention, there is provided a neutral condensation curable poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer sealant composition comprising

(a) a poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer,
(b) a cross-linker, and
(c) a condensation catalyst.

In yet another embodiment of the present invention, there is provided a method for making a neutral condensation curable poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer sealant composition which comprises

(a) effecting reaction between bis(diorganohydroxysilyl)arylene and poly(fluoroalkylorganosiloxane cyclopolyorganosiloxane to form a condensation curable poly(fluoroorganosiloxane-siloxane-poly(silylene)siloxane block copolymer,
(b) shearing the copolymer, and
(c) blending a cross-linker and a condensation catalyst with the copolymer to form a sealant.

DETAILED DESCRIPTION OF THE INVENTION

The poly(fluoro)organosiloxane-poly(silylene)siloxane block copolymers, or “block copolymers” within the scope of the present invention, can be used to make aircraft fuel tank sealants having property profiles which include a glass transition temperature (Tg) of about -54°C or below and can be made by the ring opening polymerization of a poly(fluoroalkylorganosiloxane cyclopolyorganosiloxane in the presence of a bis(diorganohydroxysilyl)arylene.

As used hereinafter, the term “bis(diorganohydroxysilyl)arylene”, or “bis(hydroxysilyl)arylene” is shown by the formula,

\[(\text{HO})_{Q1}(\text{R})_{Q2} \text{Si}(\text{R})_{Q3} \text{O}\]  

and the term “silylenesiloxy” can be represented by the formula,

\[(\text{R})_{1,4-}\text{Si}(\text{R})_{1,4-}\text{O}\]

where Q1 is a C(6.12) divalent aromatic organic radical, and Q2 is a C(1.4) alkyl radical. Preferably, the bis (diorganohydroxysilyl)arylene is 1,4-bis(dimethylhydroxysilyl)benzene.

“Poly(fluoroalkylorganosiloxane cyclopolyorganosiloxane”, sometimes expressed as “poly(fluoroalkyl)cyclic siloxane” is shown by the following formula:

\[(\text{R})_{1,4-}\text{Si}(\text{R})_{1,4-}\text{O}\]
where R is a C_{(2.12)} divalent organic radical, R is as previously defined, and X is a member selected from the group consisting of R and RO. Some of the C(2.12) divalent hydrocarbon radicals included within X are dialkylene radicals, for example, phenylene, tolylene, and naphthylene. Also included are divalent arylene radicals, for example, phenylene, tolylene, xylene, and naphthylene. Divalent aromatic radicals included within X are for example phenylene, tolylene, xylene, and naphthylene.

The cross-linker can be used in combination with an effective amount of a condensation catalyst, such as a tin compound, to effect the neutral condensation cure of block copolymers comprising blocks of poly(fluoroorgano)organosiloxane units chemically combined with poly(silylarylene)siloxane groups. The block copolymers are referred to as “poly(fluoro)siloxane-poly(silylarylene)siloxane block copolymers.”

A poly(fluoroorgano)siloxane-poly(silylarylene)siloxane block copolymer useful in making a condensation curable sealant composition was prepared as follows:

A mixture of 2.26 grams (g) (0.010 mole) of 1,2-bis(triethoxysilyl)methylene, 1,6-bis(trimethoxysilyl)hexane, 1,4-bis[(trimethoxysilyl)(ethyl)]benzene, 1,2-bis[(methyl(diethoxysilyl)]ethane, and 1,6-bis[(methyl(diethoxysilyl)]hexane. The cross-linkers are present in a range between about 1 and about 20 parts per 100 parts of block copolymer.

In order that skilled in the art will be better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight unless otherwise indicated.

**EXAMPLE 1**

A poly(fluoroorgano)siloxane-poly(silylarylene)siloxane block copolymer useful in making a condensation curable sealant composition was prepared as follows:

A mixture of 2.26 grams (g) (0.010 mole) of 1,4-bis[(dimethylhydroxysilyl)]benzene and 9.42 g (0.020 mole) of tris[(trifluoropropyl)methyl]cyclosiloxane was heated with stirring to about 150°C. Under a nitrogen atmosphere. There was then added 0.04 g of sodium fluorosilicate. After 60 minutes at 150°C, the mixture was cooled to 25°C. The reaction mixture was poured into a mixture of 2 parts per 100 parts of block copolymer, comprised of diatomaceous earth, precipitated silica, ground quartz, or calcium carbonate. It is preferred to use fumed silica which has been pretreated with an effective amount of a cyclic siloxane, such as octamethylcyclotetrasiloxane, or a mixture thereof with an organosiloxane, such as hexamethyldisilazane. The proportion of filler can be used. Preferably, the filler is present in a range between about 5 parts by weight and about 15 parts by weight per 100 parts of block copolymer. A heat stabilizer, such as iron oxide, is preferred to be about 0.1 and 10 parts by weight, per 100 parts of block copolymer has been found to be effective.

After blending of the masterbatch ingredients, the mixture can be degassed under reduced pressure, and the resulting paste can be stored.
were obtained, where the respective cross-linked condensation curves were prepared as follows from a block copolymer made in accordance with the method of Example 1. The block copolymer was initially compounded in a Baker-Perrins double-planetary mixer for 1 hour under a nitrogen blanket with a silazane octamethylcyclotetrasiloxane treated fumed silica, and red iron oxide. A homogeneous filler dispersion was prepared based on the use of 1324 parts of block copolymer, 105 parts of a bis(polyalkoxysilyl) hydrocarbon cross-linker and 0.5 part of a bis[polyalkoxysilyl]benzene, or “BTMSEB”.

Another test period, “B”, was heat aging at 177°C for 7 days after standard cure. There was also included, “C”, a viscous red sealant paste useful in making condensation curable sealant compositions which are useful as fuel resistant sealing materials, electronic encapsulation, and in applications requiring chemically resistant materials. Particularly, the crosslinkers can be used for preparation of fuel tank sealants.

The above results show that the copolymers of the present invention are depolymerization resistant and provide neutral condensation curable compositions which are useful as solvent resistant sealants.

The crosslinker in the present invention can be employed in non-corrosive cure systems to fabricate elastomers useful as fuel resistant sealing materials, electronic encapsulation, and in applications requiring chemically resistant materials.

What is claimed:

1. A condensation curable poly(fluoroorgano)siloxane-poly(silylarylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about −54°C.

2. The copolymer in accordance with claim 1, wherein the copolymer comprises the reaction product of a bis(diorganohydroxysilyl)arylene chemically combined with a poly(fluoroalkyl)arylene cycopolysiloxane.

3. The copolymer in accordance with claim 1, wherein the copolymer is depolymerization resistant.

4. The copolymer in accordance with claim 1, wherein the copolymer exhibits a weight average molecular weight in the range between about 60,000 and about 190,000.

5. The copolymer in accordance with claim 2, wherein the poly(fluoroalkyl)arylene cycopolysiloxane block copolymer is present in a range between about 0.5 moles and about 4 moles, per mole of bis(diorganohydroxysilyl)arylene.

6. The copolymer in accordance with claim 2, wherein the poly(fluoroalkyl)arylene cycopolysiloxane is present in a range between about 1 moles and about 2 moles, per mole of bis(diorganohydroxysilyl)arylene.

7. The copolymer in accordance with claim 2, wherein the bis(diorganohydroxysilyl)arylene comprises the formula

\[ \text{(HO)}_{n}R_{1}S_{i}=O_{1} \]

where \( Q^{1} \) is a \( C_{1-12} \) divalent aromatic organic radical, and \( R \) is a \( C_{1-5} \) alkyl radical.

### Example 2

A viscous red sealant paste was prepared by blending in a Semco 388 mixer, 4 parts of a bis(polyalkoxysilyl) C(2-30) hydrocarbon cross-linker and 100 parts of the above block copolymer red sealant paste contained in a Semco cartridge. The respective neutral condensation cureable sealant compositions are identified in the tables below by the particular bis(polyalkoxysilyl)Q cross-linker, where Q is as previously defined. More particularly, the bis(polyalkoxysilyl)Q cross-linkers include 1,2-bis[trimethoxysilyl]ethane, or “BTSE”, 1,6-bis(trimethoxysilyl)hexane, or “BTMSHEX”, and 1,4-bis[trimethoxysilyl(ethyl)]benzene, or “BTMSEB”.

<table>
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<tr>
<th>7 Day Test Periods</th>
<th>Tensile Strength (psi)</th>
<th>Elongation (%)</th>
<th>100% Modulus</th>
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<td>A</td>
<td>BTMSEB 250</td>
<td>196</td>
<td>104</td>
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<tr>
<td></td>
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</tr>
<tr>
<td>C</td>
<td>BTMSEB 151</td>
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The above results show that the copolymers of the present invention are depolymerization resistant and provide neutral condensation curable compositions which are useful as solvent resistant sealants. While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present invention.
8. The copolymer in accordance with claim 7, wherein the bis(diorganohydroxyaryl)arylene comprises 1,4-bis(dimethylhydroxyaryl)benzene.

9. The copolymer in accordance with claim 2, wherein the copolymer comprises the reaction product of poly(fluoroalkylorgano)cyclopolsiloxane comprises tris[(trifluoropropyl)methyl]cyclosiloxane.

10. The copolymer in accordance with claim 9, wherein the poly(fluoroalkylorgano)cyclopolsiloxane comprises the formula

$$[(R^1)(R^2)SiO]_n$$

where R^1 is a C_{3-8} polyfluoroalkyl radical, R^2 is a C_{1-12} organic radical, and “a” is an integer in a range between about 3 and about 8 inclusive.

11. A depolymerization resistant condensation curable poly(fluoroalkylorgano)siloxane-poly(silarylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about -54°C and a weight average molecular weight in the range between about 60,000 and about 190,000, wherein the copolymer comprises the reaction product of 1,4-bis(dimethylhydroxyaryl)benzene chemically combined with tris[(trifluoropropyl)methyl]cyclosiloxane.

12. A method for making a poly(fluoroalkylorgano)siloxane-poly(silarylene)siloxane copolymer comprising effecting reaction between bis(diorganohydroxyaryl)arylene and poly(fluoroalkylorgano)cyclopolsiloxane.

13. The method in accordance with claim 12, wherein the reaction is conducted at a temperature in a range between about 60°C and about 150°C.

14. The method in accordance with claim 12, wherein the reaction further comprises an initiator.

15. The method in accordance with claim 14, wherein the initiator is present in a range between about 5 parts per million and about 50 parts per million.

16. The method in accordance with claim 14, wherein the initiator comprises an alkali fluorosilanolate.

17. The method in accordance with claim 12, wherein the reaction further comprises a quencher which is present in a range between about 10 parts per million and about 60 parts per million.

18. The method in accordance with claim 16, wherein the quencher comprises a silyl phosphate.

19. The method in accordance with claim 12, wherein the bis(diorganohydroxyaryl)arylene comprises the formula

$$HO-[(R)_2Si]-Q^i,$$

where Q^i is a C_{6-12} divalent aromatic organic radical, and R is a C_{1-12} alkyl radical.

20. The method in accordance with claim 19, wherein the bis(diorganohydroxyaryl)arylene comprises 1,4-bis(dimethylhydroxyaryl)benzene.

21. The method in accordance with claim 12, wherein the poly(fluoroalkylorgano)cyclopolsiloxane comprises the formula

$$[(R^1)(R^2)SiO]_n$$

where R^1 is a C_{3-8} polyfluoroalkyl radical, R^2 is a C_{1-12} organic radical, and “a” is an integer in a range between about 3 and about 8 inclusive.

22. The method in accordance with claim 21, wherein the poly(fluoroalkylorgano)cyclopolsiloxane comprises tris[(trifluoropropyl)methyl]cyclosiloxane.

23. The method in accordance with claim 12, wherein the copolymer has a glass transition temperature not exceeding about -54°C.

24. The method in accordance with claim 12, wherein the copolymer has a weight average molecular weight in a range between about 60,000 and about 190,000.

25. A method for making a depolymerization resistant condensation curable copolymer having a glass transition temperature not exceeding about -54°C and a weight average molecular weight in the range between about 60,000 and about 190,000, comprising effecting reaction between 1,4-bis(dimethylhydroxyaryl)benzene and tris[(trifluoropropyl)methyl]cyclosiloxane in the presence of sodium fluorosilanolate and silyl phosphate at a temperature in a range between about 60°C and about 150°C.