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(54) Title: REINFORCED SILICONE RESIN FILM

(57) Abstract: A reinforced silicone resin film comprising at least two polymer layers, wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units, and at least one of the polymer layers comprises a carbon nanomaterial.

## REINFORCED SILICONE RESIN FILM

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/915,137, filed on 01 May 2007, under 35 U.S.C. §119(e). U.S. Provisional Patent Application Serial No. 60/915,137 is hereby incorporated by reference.

## FIELD OF THE INVENTION

[0002] The present invention relates to a reinforced silicone resin film and more particularly to a reinforced silicone resin film comprising at least two polymer layers, wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units, and at least one of the polymer layers comprises a carbon nanomaterial.

## BACKGROUND OF THE INVENTION

[0003] Silicone resins are useful in a variety of applications by virtue of their unique combination of properties, including high thermal stability, good moisture resistance, excellent flexibility, high oxygen resistance, low dielectric constant, and high transparency. For example, silicone resins are widely used as protective or dielectric coatings in the automotive, electronic, construction, appliance, and aerospace industries.

[0004] Although silicone resin coatings can be used to protect, insulate, or bond a variety of substrates, free standing silicone resin films have limited utility due to low tear strength, high brittleness, low glass transition temperature, and high coefficient of thermal expansion. Consequently, there is a need for free standing silicone resin films having improved mechanical and thermal properties.

## SUMMARY OF THE INVENTION

[0005] The present invention is directed to a reinforced silicone resin film comprising at least two polymer layers, wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units, and at least one of the polymer layers comprises a carbon nanomaterial.

[0006] The reinforced silicone resin film of the present invention has low coefficient of thermal expansion, and exhibits high resistance to thermally induced cracking.

[0007] The reinforced silicone resin film of the present invention is useful in applications requiring films having high thermal stability, flexibility, mechanical strength, and transparency. For example, the silicone resin film can be used as an integral component of flexible displays, solar cells, flexible electronic boards, touch screens, fire-resistant wallpaper, and impact-resistant windows. The film is also a suitable substrate for transparent or nontransparent electrodes.

#### DETAILED DESCRIPTION OF THE INVENTION

[0008] As used herein, the term “disilyloxane units” refers to organosilicon units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), where  $R^1$ , a, and b are defined below. Also, the term “mol% of disilyloxane units having the formula (I)” is defined as the ratio of the number of moles of disilyloxane units having the formula (I) in the silicone resin to the sum of the number of moles of siloxane units and disilyloxane units in the resin, multiplied by 100. Further, the term “mol% of siloxane units having the form of particles” is defined as the ratio of the number of moles of siloxane units having the form of particles in the resin to the sum of the number of moles of siloxane units and disilyloxane units in the resin, multiplied by 100.

[0009] A reinforced silicone resin film according to the present invention comprises at least two polymer layers, wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl, a is 0, 1, or 2, and b is 0, 1, 2 or 3; and at least one of the polymer layers comprises a carbon nanomaterial.

[0010] Each of the polymer layers of the reinforced silicone resin film typically has a thickness of from 0.01 to 1000  $\mu m$ , alternatively from 5 to 500  $\mu m$ , alternatively from 10 to 100  $\mu m$ .

[0011] Each of the polymer layers of the reinforced silicone resin film can comprise a thermoplastic polymer or a thermoset polymer. The thermoplastic or thermoset polymer can be a homopolymer or a copolymer. Moreover, the thermoplastic or thermoset polymer can be a silicone polymer or an organic polymer. As used herein and below, the term “thermoplastic polymer” refers to a polymer that has the property of converting to a fluid (flowable) state

when heated and of becoming rigid (nonflowable) when cooled. Also, the term “thermoset polymer” refers to a cured (i.e., cross-linked) polymer that does not convert to a fluid state on heating.

**[0012]** Examples of thermoplastic polymers include, but are not limited to thermoplastic silicone polymers such as poly(diphenylsiloxane-*co*-phenylmethylsiloxane); and thermoplastic organic polymers such as polyolefins, polysulfones, polyacrylates and polyetherimides.

**[0013]** Examples of thermoset polymers include, but are not limited to, thermoset silicone polymers such as cured silicone elastomers, silicone gels, and cured silicone resins; and thermoset organic polymers such as epoxy resins, cured amino resins, cured polyurethanes, cured polyimides, cured phenolic resins, cured cyanate ester resins, cured bismaleimide resins, cured polyesters, and cured acrylic resins.

**[0014]** Adjacent polymer layers of the reinforced silicone resin film differ in at least one of numerous physical and chemical properties, including thickness, polymer composition, cross-link density, and concentration of carbon nanomaterial or other reinforcement.

**[0015]** The reinforced silicone resin film typically comprises from 1 to 100 polymer layers, alternatively from 1 to 10 polymer layers, alternatively from 2 to 5 polymer layers.

**[0016]** At least one of the polymer layers of the reinforced silicone resin film comprises a cured product of at least one silicone resin comprising disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl, a is 0, 1, or 2, and b is 0, 1, 2 or 3. As used herein, the term “cured product of at least one silicone resin” refers to a cross-linked product of at least one silicone resin, the product having a three-dimensional network structure. The silicone resin, methods of preparing the resin, and methods of preparing the cured product of the silicone resin are described below in the method of preparing the reinforced silicone resin film of the present invention.

**[0017]** At least one of the polymer layers of the reinforced silicone resin film comprises a carbon nanomaterial. The carbon nanomaterial can be any carbon material having at least one physical dimension (e.g., particle diameter, fiber diameter, layer thickness) less than about 200 nm. Examples of carbon nanomaterials include, but are not limited to, carbon nanoparticles having three dimensions less than about 200 nm, such as quantum dots, hollow spheres, and fullerenes; fibrous carbon nanomaterials having two dimensions less than about

200 nm, such as nanotubes (e.g., single-walled nanotubes and multi-walled nanotubes) and nanofibers (e.g., axially aligned, platelet, and herringbone or fishbone nanofibers); and layered carbon nanomaterials having one dimension less than about 200 nm, such as carbon nanoplatelets (e.g., exfoliated graphite and graphene sheet). The carbon nanomaterial can be electrically conductive or semiconductive.

**[0018]** The carbon nanomaterial can also be an oxidized carbon nanomaterial, prepared by treating the aforementioned carbon nanomaterials with an oxidizing acid or mixture of acids at elevated temperature. For example, the carbon nanomaterial can be oxidized by heating the material in a mixture of concentrated nitric and concentrated sulfuric acid (1:3 v/v, 25 mL/g carbon) at a temperature of from 40 to 150 °C for 1-3 hours.

**[0019]** The carbon nanomaterial can be a single carbon nanomaterial or a mixture comprising at least two different carbon nanomaterials, each as described above.

**[0020]** The concentration of the carbon nanomaterial in the polymer layer is typically from 0.0001 to 99% (w/w), alternatively from 0.001 to 50% (w/w), alternatively from 0.01 to 25% (w/w), alternatively from 0.1 to 10% (w/w), alternatively from 1 to 5% (w/w), based on the total weight of the polymer layer.

**[0021]** Methods of preparing carbon nanomaterials are well-known in the art. For example, carbon nanoparticles (e.g., fullerenes) and fibrous carbon nanomaterials (e.g., nanotubes, and nanofibers) can be prepared using at least one of the following methods: arc discharge, laser ablation, and catalytic chemical vapor deposition. In the arc discharge process, an arc discharge between two graphite rods produces, depending on the gas atmosphere, single-walled nanotubes, multi-walled nanotubes, and fullerenes. In the laser ablation method, a graphite target loaded with a metal catalyst is irradiated with a laser in a tube furnace to produce single- and multi-walled nanotubes. In the catalytic chemical vapor deposition method, a carbon-containing gas or gas mixture is introduced into a tube furnace containing a metal catalyst at a temperature of from 500 to 1000 °C (and different pressures) to produce carbon nanotubes and nanofibers. Carbon nanoplatelets can be prepared by the intercalation and exfoliation of graphite.

**[0022]** In addition to a thermoplastic or thermoset polymer, at least one of the polymer layers of the reinforced silicone resin film can further comprise a reinforcement selected from a carbon nanomaterial, a fiber reinforcement, and a mixture thereof.

[0023] The fiber reinforcement can be any reinforcement comprising fibers, provided the reinforcement has a high modulus and high tensile strength. The fiber reinforcement typically has a Young's modulus at 25 °C of at least 3 GPa. For example, the reinforcement typically has a Young's modulus at 25 °C of from 3 to 1,000 GPa, alternatively from 3 to 200 GPa, alternatively from 10 to 100 GPa. Moreover, the reinforcement typically has a tensile strength at 25 °C of at least 50 MPa. For example, the reinforcement typically has a tensile strength at 25 °C of from 50 to 10,000 MPa, alternatively from 50 to 1,000 MPa, alternatively from 50 to 500 MPa.

[0024] The fiber reinforcement can be a woven fabric, e.g., a cloth; a nonwoven fabric, e.g., a mat or roving; or loose (individual) fibers. The fibers in the reinforcement are typically cylindrical in shape and have a diameter of from 1 to 100  $\mu\text{m}$ , alternatively from 1 to 20  $\mu\text{m}$ , alternatively from 1 to 10  $\mu\text{m}$ . Loose fibers may be continuous, meaning the fibers extend throughout the reinforced silicone resin film in a generally unbroken manner, or chopped.

[0025] The fiber reinforcement is typically heat-treated prior to use to remove organic contaminants. For example, the fiber reinforcement is typically heated in air at an elevated temperature, for example, 575 °C, for a suitable period of time, for example 2 h.

[0026] Examples of fiber reinforcements include, but are not limited to reinforcements comprising glass fibers; quartz fibers; graphite fibers; nylon fibers; polyester fibers; aramid fibers, such as Kevlar® and Nomex®; polyethylene fibers; polypropylene fibers; and silicon carbide fibers.

[0027] The concentration of the fiber reinforcement in the polymer layer is typically from 0.1 to 95% (w/w), alternatively from 5 to 75% (w/w), alternatively from 10 to 40% (w/w), based on the total weight of the polymer layer.

[0028] When one or more of the polymer layers of the reinforced silicone resin film comprise a mixture of a carbon nanomaterial and a fiber reinforcement, the concentration of the mixture is typically from 0.1 to 96% (w/w), alternatively from 5 to 75% (w/w), alternatively from 10 to 40% (w/w), based on the total weight of the polymer layer.

[0029] The polymer layers of the reinforced silicone resin film can be prepared as described below in the method of preparing the reinforced silicone resin film of the present invention.

[0030] The reinforced silicone resin film can be prepared by a method comprising:  
forming a first polymer layer; and

forming at least one additional polymer layer on the first polymer layer; wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units, and at least one of the polymer layers comprises a carbon nanomaterial. The first polymer layer and the additional polymer layer(s) are as described and exemplified above for the polymer layers of the reinforced silicone resin film.

**[0031]** In the first step of the method of preparing the reinforced silicone resin film, a first polymer layer is formed on a release liner.

**[0032]** The release liner can be any rigid or flexible material having a surface from which the first polymer layer can be removed without damage. Examples of release liners include, but are not limited to, silicon, quartz; fused quartz; aluminum oxide; ceramics; glass; metal foils; polyolefins such as polyethylene, polypropylene, polystyrene, and polyethyleneterephthalate; fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride; polyamides such as Nylon; polyimides; polyesters such as poly(methyl methacrylate); epoxy resins; polyethers; polycarbonates; polysulfones; and polyether sulfones. The release liner can also be a material, as exemplified above, having a surface treated with a release agent, such as a silicone release agent.

**[0033]** The first polymer layer can be formed using a variety of methods, depending on the composition of the polymer layer. For example, when the first polymer layer comprises a thermoplastic polymer, the layer can be formed by (i) coating a release liner with a composition comprising a thermoplastic polymer in a fluid state and (ii) converting the thermoplastic polymer of the coated release liner to a solid state.

**[0034]** In step (i) of the preceding method of forming the first polymer layer, a release liner, described above, is coated with a composition comprising a thermoplastic polymer in fluid state.

**[0035]** The composition comprising a thermoplastic polymer can be any composition comprising a thermoplastic polymer in a fluid (i.e., liquid) state. As used herein, the term "thermoplastic polymer in a fluid state" means the polymer is in a molten state or dissolved in an organic solvent. For example, the composition can comprise a thermoplastic polymer in a molten state above the melting point ( $T_m$ ) or glass transition temperature ( $T_g$ ) of the polymer, or the composition can comprise a thermoplastic polymer and an organic solvent.

**[0036]** The thermoplastic polymer of the composition is as described and exemplified above for the first reinforced silicone resin film. The thermoplastic polymer can be a single

thermoplastic polymer or a mixture (i.e., blend) comprising two or more different thermoplastic polymers. For example, the thermoplastic polymer can be a polyolefin blend.

**[0037]** The organic solvent can be any protic, aprotic, or dipolar aprotic organic solvent that does not react with the thermoplastic polymer and is miscible with the polymer. Examples of organic solvents include, but are not limited to, saturated aliphatic hydrocarbons such as n-pentane, hexane, n-heptane, isooctane and dodecane; cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene and mesitylene; cyclic ethers such as tetrahydrofuran (THF) and dioxane; ketones such as methyl isobutyl ketone (MIBK); halogenated alkanes such as trichloroethane; halogenated aromatic hydrocarbons such as bromobenzene and chlorobenzene; and alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-butanol, 1,1-dimethyl-1-ethanol, pentanol, hexanol, cyclohexanol, heptanol, and octanol.

**[0038]** The organic solvent can be a single organic solvent or a mixture comprising two or more different organic solvents, each as described and exemplified above.

**[0039]** The composition comprising the thermoplastic polymer can further comprise a carbon nanomaterial, described and exemplified above.

**[0040]** The release liner can be coated with the composition comprising a thermoplastic polymer in a fluid state using conventional coating techniques, such as spin coating, dipping, spraying, brushing, extrusion, or screen-printing. The amount of the composition is sufficient to form a first polymer layer having a thickness of from 0.01 to 1000  $\mu\text{m}$ .

**[0041]** In step (ii) of the preceding method, the thermoplastic polymer of the coated release liner is converted to a solid state. When the composition used to coat the release liner comprises a thermoplastic polymer in a molten state, the thermoplastic polymer can be converted to a solid state by allowing the polymer to cool to a temperature below the liquid-solid transition temperature ( $T_g$  or  $T_m$ ), for example, room temperature. When the composition used to coat the release liner comprises a thermoplastic polymer and an organic solvent, the thermoplastic polymer can be converted to a solid state by removing at least a portion of the solvent. The organic solvent can be removed by allowing the solvent to evaporate at ambient temperature or by heating the coating to a moderate temperature, for example, below the solid-liquid transition temperature of the polymer.

**[0042]** The method of forming the first polymer layer, wherein the layer comprises a thermoplastic polymer, can further comprise, after step (i) and before step (ii), applying a

second release liner to the coated release liner of the first step to form an assembly, and compressing the assembly. The assembly can be compressed to remove excess composition and/or entrapped air, and to reduce the thickness of the coating. The assembly can be compressed using conventional equipment such as a stainless steel roller, hydraulic press, rubber roller, or laminating roll set. The assembly is typically compressed at a pressure of from 1,000 Pa to 10 MPa and at a temperature of from room temperature ( $\sim 23 \pm 2$  °C) to 200 °C.

**[0043]** The method of forming the first polymer layer, wherein the layer comprises a thermoplastic polymer, can further comprise repeating the steps (i) and (ii) to increase the thickness of the polymer layer, provided the same composition is used for each coating step.

**[0044]** When the first polymer layer comprises a thermoset (i.e., cross-linked) polymer, the layer can be formed by (i) coating a release liner with a curable composition comprising a thermosetting polymer and (ii) curing the thermosetting polymer of the coated release liner.

**[0045]** In step (i) of the immediately preceding method of forming the first polymer layer, a release liner, described above, is coated with a curable composition comprising a thermosetting polymer.

**[0046]** The curable composition comprising a thermosetting polymer can be any curable composition containing a thermosetting polymer. As used herein and below, the term “thermosetting polymer” refers to a polymer having the property of becoming permanently rigid (nonflowable) when cured (i.e., cross-linked). The curable composition typically contains a thermosetting polymer and additional ingredients, such as an organic solvent, cross-linking agent, and/or catalyst.

**[0047]** Examples of curable compositions comprising thermosetting polymers include, but are not limited to, curable silicone compositions, such as hydrosilylation-curable silicone compositions, condensation-curable silicone compositions, and peroxide-curable silicone compositions; curable polyolefin compositions such as polyethylene and polypropylene compositions; curable polyamide compositions; curable epoxy resin compositions; curable amino resin compositions; curable polyurethane compositions; curable polyimide compositions; curable polyester compositions; and curable acrylic resin compositions.

**[0048]** The curable composition comprising a thermosetting polymer can also be a curable silicone composition comprising (A) a silicone resin comprising disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), wherein each  $R^1$  is independently -H,

hydrocarbyl, or substituted hydrocarbyl, a is 0, 1, or 2, and b is 0, 1, 2 or 3; and (B) an organic solvent.

**[0049]** Component (A) is at least one silicone resin comprising disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl; a is 0, 1, or 2; and b is 0, 1, 2 or 3.

**[0050]** The hydrocarbyl groups represented by  $R^1$  typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms. Acyclic hydrocarbyl groups containing at least three carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl and xylyl; arakyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl; aralkenyl, such as styryl and cinnamyl; and alkynyl, such as ethynyl and propynyl.

**[0051]** The substituted hydrocarbyl groups represented by  $R^1$  can contain one or more of the same or different substituents, provided the substituent does not prevent formation of the alcoholysis product, the hydrolyzate, or the silicone resin. Examples of substituents include, but are not limited to, -F, -Cl, -Br, -I, -OH,  $-OR^2$ ,  $-OCH_2CH_2OR^3$ ,  $-CO_2R^3$ ,  $-OC(=O)R^2$ ,  $-C(=O)NR^3_2$ , wherein  $R^2$  is  $C_1$  to  $C_8$  hydrocarbyl and  $R^3$  is  $R^2$  or -H.

**[0052]** The hydrocarbyl groups represented by  $R^2$  typically have from 1 to 8 carbon atoms, alternatively from 3 to 6 carbon atoms. Acyclic hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl include, but are not limited to, unbranched and branched alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, and octyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; phenyl; alkaryl, such as tolyl and xylyl; aralkyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl; arylalkenyl, such as styryl; and alkynyl, such as ethynyl and propynyl.

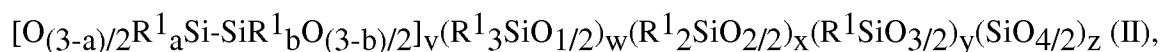
**[0053]** The silicone resin typically comprises at least 1 mol% of disilyloxane units having the formula (I). For example, the silicone resin typically comprises from 1 to 100 mol%, alternatively from 5 to 75 mol%, alternatively from 10 to 50 mol%, of disilyloxane units having the formula (I).

**[0054]** In addition to disilyloxane units having the formula (I), the silicone resin may contain up to 99 mol% of other siloxane units. Examples of other siloxane units include, but are not limited to, siloxane units having formulae selected from:  $R^1_3SiO_{1/2}$ ,  $R^1_2SiO_{2/2}$ ,  $R^1SiO_{3/2}$ , and  $SiO_{4/2}$ , wherein  $R^1$  is as described and exemplified above.

**[0055]** The silicone resin typically has a number-average molecular weight of from 200 to 500,000, alternatively from 500 to 150,000, alternatively from 1,000 to 75,000, alternatively from 2,000 to 12,000, wherein the molecular weight is determined by gel permeation chromatography using a refractive index detector and polystyrene standards.

**[0056]** The silicone resin typically contains from 1 to 50% (w/w), alternatively from 5 to 50% (w/w), alternatively from 5 to 35% (w/w), alternatively from 10% to 35% (w/w), alternatively from 10 to 20% (w/w), of silicon-bonded hydroxy groups based on the total weight of the resin, as determined by  $^{29}Si$  NMR.

**[0057]** According to a first embodiment, the silicone resin has the formula:



wherein each  $R^1$  is independently  $-H$ , hydrocarbyl, or substituted hydrocarbyl; a is 0, 1, or 2; b is 0, 1, 2 or 3; v is from 0.01 to 1; w is from 0 to 0.84; x is from 0 to 0.99; y is from 0 to 0.99; z is from 0 to 0.95; and  $v+w+x+y+z = 1$ .

**[0058]** The hydrocarbyl and substituted hydrocarbyl groups represented by  $R^1$  are as described and exemplified above.

**[0059]** In the formula (II) of the silicone resin, the subscripts v, w, x, y, and z are mole fractions. The subscript v typically has a value of from 0.01 to 1, alternatively from 0.2 to 0.8, alternatively from 0.3 to 0.6; the subscript w typically has a value of from 0 to 0.84, alternatively from 0.1 to 0.6, alternatively from 0.2 to 0.4; the subscript x typically has a value of from 0 to 0.99, alternatively from 0.1 to 0.8, alternatively from 0.2 to 0.6; the subscript y typically has a value of from 0 to 0.99, alternatively from 0.2 to 0.8, alternatively from 0.4 to 0.6; and the subscript z typically has a value of from 0 to 0.95, alternatively from 0.1 to 0.7, alternatively from 0.2 to 0.5.

**[0060]** Examples of silicone resins having the formula (II) include, but are not limited to, resins having the following formulae:  $(O_{2/2}MeSiSiO_{3/2})_{0.1}(PhSiO_{3/2})_{0.9}$ ,  $(O_{2/2}MeSiSiMeO_{2/2})_{0.2}(Me_2SiO_{2/2})_{0.1}(PhSiO_{3/2})_{0.7}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.1}(O_{2/2}MeSiSiMeO_{2/2})_{0.15}(Me_2SiO_{2/2})_{0.1}(MeSiO_{3/2})_{0.65}$ ,  $(O_{1/2}Me_2SiSiO_{3/2})_{0.25}(SiO_{4/2})_{0.5}(MePhSiO_{2/2})_{0.25}$ ,  $(O_{2/2}EtSiSiEtO_{1/2})_{0.1}(O_{2/2}MeSiSiO_{3/2})_{0.15}(Me_3SiO_{1/2})_{0.05}(PhSiO_{3/2})_{0.5}(SiO_{4/2})_{0.2}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.3}(PhSiO_{3/2})_{0.7}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.4}(MeSiO_{3/2})_{0.6}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.5}(Me_2SiO_{2/2})_{0.5}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.6}(Me_2SiO_{2/2})_{0.4}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.7}(Me_2SiO_{2/2})_{0.3}$ ,  $(O_{3/2}SiSiMe_2O_{1/2})_{0.75}(PhSiO_{3/2})_{0.25}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.75}(SiO_{4/2})_{0.25}$ ,  $(O_{2/2}MeSiSiMe_2O_{1/2})_{0.5}(O_{2/2}MeSiSiO_{3/2})_{0.3}(PhSiO_{3/2})_{0.2}$ ,  $(O_{2/2}EtSiSiMeO_{2/2})_{0.8}(MeSiO_{3/2})_{0.05}(SiO_{4/2})_{0.15}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.8}(Me_3SiO_{1/2})_{0.05}(Me_2SiO_{2/2})_{0.1}(SiO_{4/2})_{0.5}$ ,  $(O_{2/2}MeSiSiEtO_{2/2})_{0.25}(O_{3/2}SiSiMeO_{2/2})_{0.6}(MeSiO_{3/2})_{0.1}(SiO_{4/2})_{0.05}$ ,  $(O_{1/2}Me_2SiSiMeO_{2/2})_{0.75}(O_{2/2}MeSiSiMeO_{2/2})_{0.25}$ ,  $(O_{1/2}Et_2SiSiEtO_{2/2})_{0.5}(O_{2/2}EtSiSiEtO_{2/2})_{0.5}$ ,  $(O_{1/2}Et_2SiSiEtO_{2/2})_{0.2}(O_{2/2}MeSiSiMeO_{2/2})_{0.8}$ , and  $(O_{1/2}Me_2SiSiMeO_{2/2})_{0.6}(O_{2/2}EtSiSiEtO_{2/2})_{0.4}$ , where Me is methyl, Et is ethyl, Ph is phenyl, the resin contains siloxane units in the form of particles, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

**[0061]** The silicone resin of the first embodiment can be prepared by (i) reacting at least one halodisilane having the formula  $Z_{3-a}R^1_aSi-SiR^1_bZ_{3-b}$  and, optionally, at least one halosilane having the formula  $R^1_bSiZ_{4-b}$  with at least one alcohol having the formula  $R^4OH$  in the presence of an organic solvent to produce an alcoholysis product, wherein each  $R^1$  is independently  $-H$ , hydrocarbyl, or substituted hydrocarbyl,  $R^4$  is alkyl or cycloalkyl, Z is halo,  $a = 0, 1, \text{ or } 2$ , and  $b = 0, 1, 2 \text{ or } 3$ ; (ii) reacting the alcoholysis product with water at a temperature of from 0 to 40 °C to produce a hydrolyzate; and (iii) heating the hydrolyzate to produce the resin.

**[0062]** In step (i) of the method of preparing the silicone resin at least one halodisilane having the formula  $Z_{3-a}R^1_aSi-SiR^1_bZ_{3-b}$  and, optionally, at least one halosilane having the formula  $R^1_bSiZ_{4-b}$  are reacted with at least one alcohol having the formula  $R^4OH$  in the

presence of an organic solvent to produce an alcoholysis product, wherein each  $R^1$  is independently  $-H$ , hydrocarbyl, or substituted hydrocarbyl,  $R^4$  is alkyl or cycloalkyl,  $Z$  is halo,  $a = 0, 1, \text{ or } 2$ , and  $b = 0, 1, 2 \text{ or } 3$ . As used herein, the term "alcoholysis product" refers to a product formed by replacement of the silicon-bonded halogen atom(s) in the halodisilane and, when present, the halosilane with the group  $-OR^4$ , wherein  $R^4$  is as described and exemplified below.

**[0063]** The halodisilane is at least one halodisilane having the formula  $Z_{3-a}R^1_aSi-SiR^1_bZ_{3-b}$ , wherein  $R^1$  is as described and exemplified above,  $Z$  is halo,  $a = 0, 1, \text{ or } 2$ , and  $b = 0, 1, 2 \text{ or } 3$ . Examples of halo atoms represented by  $Z$  include  $-F$ ,  $-Cl$ ,  $-Br$ , and  $-I$ .

**[0064]** Examples of halodisilanes include, but are not limited to, disilanes having the formulae:  $Cl_2MeSiSiMeCl_2$ ,  $Cl_2MeSiSiMe_2Cl$ ,  $Cl_3SiSiMeCl_2$ ,  $Cl_2EtSiSiEtCl_2$ ,  $Cl_2EtSiSiEt_2Cl$ ,  $Cl_3SiSiEtCl_2$ ,  $Cl_3SiSiCl_3$ ,  $Br_2MeSiSiMeBr_2$ ,  $Br_2MeSiSiMe_2Br$ ,  $Br_3SiSiMeBr_2$ ,  $Br_2EtSiSiEtBr_2$ ,  $Br_2EtSiSiEt_2Br$ ,  $Br_3SiSiEtBr_2$ ,  $Br_3SiSiBr_3$ ,  $I_2MeSiSiMeI_2$ ,  $I_2MeSiSiMe_2I$ ,  $I_3SiSiMeI_2$ ,  $I_2EtSiSiEtI_2$ ,  $I_2EtSiSiEt_2I$ ,  $I_3SiSiEtI_2$ , and  $I_3SiSiI_3$ , where  $Me$  is methyl and  $Et$  is ethyl.

**[0065]** The halodisilane can be a single halodisilane or a mixture comprising two or more different halodisilanes, each having the formula  $Z_{3-a}R^1_aSi-SiR^1_bZ_{3-b}$ , wherein  $R^1$ ,  $Z$ ,  $a$ , and  $b$  are as described and exemplified above.

**[0066]** Methods of preparing halodisilanes are well known in the art; many of these compounds are commercially available. Also, the halodisilane can be obtained from the residue having a boiling point greater than  $70^\circ C$  produced in the Direct Process for making methylchlorosilanes, as taught in WO 03/099828. Fractional distillation of the Direct Process residue gives a methylchlorodisilane stream containing a mixture of chlorodisilanes.

**[0067]** The optional halosilane is at least one halosilane having the formula  $R^1_bSiZ_{4-b}$ , wherein  $R^1$ ,  $Z$ , and  $b$  are as described and exemplified above.

**[0068]** Examples of halosilanes include, but are not limited to, silanes having the formulae:  $SiCl_4$ ,  $SiBr_4$ ,  $HSiCl_3$ ,  $HSiBr_3$ ,  $MeSiCl_3$ ,  $EtSiCl_3$ ,  $MeSiBr_3$ ,  $EtSiBr_3$ ,  $Me_2SiCl_2$ ,  $Et_2SiCl_2$ ,  $Me_2SiBr_2$ ,  $Et_2SiBr_2$ ,  $Me_3SiCl$ ,  $Et_3SiCl$ , and  $Me_3SiBr$ ,  $Et_3SiBr$ , where  $Me$  is methyl and  $Et$  is ethyl.

[0069] The halosilane can be a single halosilane or a mixture comprising two or more different halosilanes, each having the formula  $R^1_bSiZ_{4-b}$ , wherein  $R^1$ , Z, and b are as described and exemplified above. Further, methods of preparing halosilanes are well known in the art; many of these compounds are commercially available.

[0070] The alcohol is at least one alcohol having the formula  $R^4OH$ , wherein  $R^4$  is alkyl or cycloalkyl. The structure of the alcohol can be linear or branched. Also, the hydroxy group in the alcohol may be attached to a primary, secondary or tertiary carbon atom.

[0071] The alkyl groups represented by  $R^4$  typically have from 1 to 8 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms. Alkyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, and octyl.

[0072] The cycloalkyl groups represented by  $R^4$  typically have from 3 to 12 carbon atoms, alternatively from 4 to 10 carbon atoms, alternatively from 5 to 8 carbon atoms. Examples of cycloalkyl groups include, but are not limited to, cyclopentyl, cyclohexyl, and methylcyclohexyl.

[0073] Examples of alcohols include, but are not limited to, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-butanol, 1,1-dimethyl-1-ethanol, pentanol, hexanol, cyclohexanol, heptanol, and octanol. The alcohol can be a single alcohol or a mixture comprising two or more different alcohols, each as described and exemplified above.

[0074] The organic solvent can be any aprotic or dipolar aprotic organic solvent that does not react with the halodisilane, the halosilane, or the silicone resin product under the conditions of the present method, and is miscible with the halodisilane, the halosilane, and the silicone resin. The organic solvent can be immiscible or miscible with water. As used herein, the term "immiscible" means that the solubility of water in the solvent is less than about 0.1 g/100 g of solvent at 25 °C. The organic solvent can also be the alcohol having the formula  $R^4OH$ , wherein  $R^4$  is as described and exemplified above, that is reacted with the halodisilane and, optionally, the halosilane.

**[0075]** Examples of organic solvents include, but are not limited to, saturated aliphatic hydrocarbons such as n-pentane, hexane, n-heptane, isooctane and dodecane; cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene and mesitylene; cyclic ethers such as tetrahydrofuran (THF) and dioxane; ketones such as methyl isobutyl ketone (MIBK); halogenated alkanes such as trichloroethane; halogenated aromatic hydrocarbons such as bromobenzene and chlorobenzene; and alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-butanol, 1,1-dimethyl-1-ethanol, pentanol, hexanol, cyclohexanol, heptanol, and octanol.

**[0076]** The organic solvent can be a single organic solvent or a mixture comprising two or more different organic solvents, each as described and exemplified above.

**[0077]** The reaction of the halodisilane and the optional halosilane with the alcohol to produce the alcoholysis product can be carried out in any standard reactor suitable for contacting, for example, halosilanes with alcohol. Suitable reactors include glass and Teflon-lined glass reactors. Preferably, the reactor is equipped with a means of agitation, such as stirring.

**[0078]** The halodisilane, the optional halosilane, the alcohol, and the organic solvent can be combined in any order. Typically, the halodisilane and optional halosilane are combined with the alcohol in the presence of the organic solvent by adding the alcohol to a mixture of the halodisilane, optional halosilane, and organic solvent. Reverse addition, i.e., addition of the silane(s) to the alcohol is also possible. The hydrogen halide gas (e.g., HCl) produced as a by-product in the reaction is typically allowed to pass from the reaction vessel into an acid neutralization trap.

**[0079]** The rate of addition of the alcohol to the halodisilane and the optional halosilane is typically from 5 mL/min. to 50 mL/min. for a 1000-mL reaction vessel equipped with an efficient means of stirring. When the rate of addition is too slow, the reaction time is unnecessarily prolonged. When the rate of addition is too fast, the violent evolution of hydrogen halide gas may be hazardous.

**[0080]** The reaction of the halodisilane and the optional halosilane with the alcohol is typically carried out at room temperature ( $\sim 23 \pm 2$  °C). However, the reaction can be carried out at lower or higher temperatures. For example, the reaction can be carried out at a temperature of from 10 °C to 60 °C.

**[0081]** The reaction time depends on several factors, including the structures of the halodisilane and the optional halosilane, and the temperature. The reaction is typically carried out for an amount of time sufficient to complete alcoholysis of the halodisilane and the optional halosilane. As used herein, the term “to complete alcoholysis” means that at least 85 mol% of the silicon-bonded halogen atoms originally present in the halodisilane and the optional halosilane combined are replaced with the group  $-OR^4$ . For example, the reaction time is typically from 5 to 180 min., alternatively from 10 to 60 min., alternatively from 15 to 25 min., at a temperature of from 10 to 60 °C. The optimum reaction time can be determined by routine experimentation using the methods set forth in the Examples section below.

**[0082]** The concentration of the halodisilane in the reaction mixture is typically from 5 to 95% (w/w), alternatively from 20 to 70% (w/w), alternatively from 40 to 60% (w/w), based on the total weight of the reaction mixture.

**[0083]** The mole ratio of the halosilane to the halodisilane is typically from 0 to 99, alternatively from 0.5 to 80, alternatively from 0.5 to 60, alternatively from 0.5 to 40, alternatively from 0.5 to 20, alternatively from 0.5 to 2.

**[0084]** The mole ratio of the alcohol to the silicon-bonded halogen atoms in the halodisilane and the halosilane combined is typically from 0.5 to 10, alternatively from 1 to 5, alternatively from 1 to 2.

**[0085]** The concentration of the organic solvent is typically from 0 to 95% (w/w), alternatively from 5 to 88% (w/w), alternatively from 30 to 82% (w/w), based on the total weight of the reaction mixture.

**[0086]** In step (ii) of the method, the alcoholysis product is reacted with water at a temperature of from 0 to 40 °C to produce a hydrolyzate.

**[0087]** The alcoholysis product is typically combined with water by adding the alcoholysis product to the water. Reverse addition, i.e., addition of water to the alcoholysis product is also possible. However, reverse addition may result in formation of predominately gels.

**[0088]** The rate of addition of the alcoholysis product to water is typically from 2 mL/min. to 100 mL/min. for a 1000-mL reaction vessel equipped with an efficient means of stirring. When the rate of addition is too slow, the reaction time is unnecessarily prolonged. When the rate of addition is too fast, the reaction mixture may form a gel.

**[0089]** The reaction of step (ii) is typically carried out at a temperature of from 0 to 40 °C, alternatively from 0 to 20 °C, alternatively from 0 to 5 °C. When the temperature is less than 0 °C, the rate of the reaction is typically very slow. When the temperature is greater than 40 °C, the reaction mixture may form a gel.

**[0090]** The reaction time depends on several factors, including the structure of the alcoholysis product and the temperature. The reaction is typically carried out for an amount of time sufficient to complete hydrolysis of the alcoholysis product. As used herein, the term “to complete hydrolysis” means that at least 85 mol% of the silicon-bonded groups  $-OR^4$  originally present in the alcoholysis product are replaced with hydroxy groups. For example, the reaction time is typically from 0.5 min. to 5 h, alternatively from 1 min. to 3 h, alternatively from 5 min. to 1 h at a temperature of from 0 to 40 °C. The optimum reaction time can be determined by routine experimentation using the methods set forth in the Examples section below.

**[0091]** The concentration of water in the reaction mixture is typically sufficient to effect hydrolysis of the alcoholysis product. For example, the concentration of water is typically from 1 mole to 50 moles, alternatively from 5 moles to 20 moles, alternatively from 8 moles to 15 moles, per mole of the silicon-bonded groups  $-OR^4$  in the alcoholysis product.

**[0092]** In step (iii) of the method of preparing the silicone resin, the hydrolyzate is heated to produce the silicone resin. The hydrolyzate is typically heated at a temperature of from 40 to 100 °C, alternatively from 50 to 85 °C, alternatively from 55 to 70 °C. The hydrolyzate is typically heated for a period of time sufficient to produce a silicone resin having a number-average molecular weight of from 200 to 500,000. For example, the hydrolyzate is typically heated for a period of from 1 h to 2 h, at a temperature of from 55 °C to 70 °C.

**[0093]** The method can further comprise recovering the silicone resin. When the mixture of step (iii) contains a water-immiscible organic solvent, such as tetrahydrofuran, the silicone resin can be recovered from the reaction mixture by separating the organic phase containing the resin from the aqueous phase. The separation can be carried out by discontinuing agitation of the mixture, allowing the mixture to separate into two layers, and removing the aqueous or organic phase. The organic phase is typically washed with water. The water can further comprise a neutral inorganic salt, such as sodium chloride, to minimize formation of an emulsion between the water and organic phase during washing. The concentration of the neutral inorganic salt in the water can be up to saturation. The organic phase can be washed

by mixing it with water, allowing the mixture to separate into two layers, and removing the aqueous layer. The organic phase is typically washed from 1 to 5 times with separate portions of water. The volume of water per wash is typically from 0.5 to 2 times the volume of the organic phase. The mixing can be carried out by conventional methods, such as stirring or shaking. The silicone resin can be used without further isolation or purification or the resin can be separated from most of the solvent by conventional methods of evaporation.

**[0094]** When the mixture of step (iii) contains a water-miscible organic solvent (e.g., methanol), the silicone resin can be recovered from the reaction mixture by separating the resin from the aqueous solution. For example, the separation can be carried out by distilling the mixture at atmospheric or subatmospheric pressure. The distillation is typically carried out at a temperature of from 40 to 60 °C, alternatively from 60 to 80 °C, at a pressure of 0.5 kPa.

**[0095]** Alternatively, the silicone resin can be separated from the aqueous solution by extracting the mixture containing the resin with a water immiscible organic solvent, such as methyl isobutyl ketone. The silicone resin can be used without further isolation or purification or the resin can be separated from most of the solvent by conventional methods of evaporation.

**[0096]** According to a second embodiment, the silicone resin comprises disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), and siloxane units having the form of particles, wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl; a is 0, 1, or 2; and b is 0, 1, 2 or 3. The hydrocarbyl and substituted hydrocarbyl groups represented by  $R^1$  are as described and exemplified above.

**[0097]** The silicone resin of the second embodiment comprises both disilyloxane units having the formula (I) and siloxane units having the form of particles. The silicone resin typically comprises at least 1 mol% of disilyloxane units having the formula (I). For example, the silicone resin typically comprises from 1 to 99 mol%, alternatively from 10 to 70 mol%, alternatively from 20 to 50 mol%, of disilyloxane units having the formula (I).

**[0098]** In addition to disilyloxane units having the formula (I), the silicone resin of the second embodiment typically comprises up to 99 mol% of siloxane units having the form of particles. For example, the silicone resin typically contains from 0.0001 to 99 mol%, alternatively from 1 to 80 mol%, alternatively from 10 to 50 mol%, of siloxane units having

the form of particles. The composition and properties of the particles are described below in the method of preparing the silicone resin.

**[0099]** In addition to units having formulae (I) and siloxane units having the form of particles, the silicone resin of the second embodiment may contain up to 98.9 mol%, alternatively up to 90 mol%, alternatively up to 60 mol%, of other siloxane units (i.e., siloxane units not having the form of particles). Examples of other siloxane units include, but are not limited to, units having formulae selected from:  $R^1_3SiO_{1/2}$ ,  $R^1_2SiO_{2/2}$ ,  $R^1SiO_{3/2}$ , and  $SiO_{4/2}$ , wherein  $R^1$  is as described and exemplified above.

**[0100]** Examples of silicone resins according to the second embodiment include, but are not limited to, resins having the following formulae:  $(O_{2/2}MeSiSiO_{3/2})_{0.1}(PhSiO_{3/2})_{0.9}$ ,  $(O_{2/2}MeSiSiMeO_{2/2})_{0.2}(Me_2SiO_{2/2})_{0.1}(PhSiO_{3/2})_{0.7}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.1}(O_{2/2}MeSiSiMeO_{2/2})_{0.15}(Me_2SiO_{2/2})_{0.1}(MeSiO_{3/2})_{0.65}$ ,  $(O_{1/2}Me_2SiSiO_{3/2})_{0.25}(SiO_{4/2})_{0.5}(MePhSiO_{2/2})_{0.25}$ ,  $(O_{2/2}EtSiSiEt_2O_{1/2})_{0.1}(O_{2/2}MeSiSiO_{3/2})_{0.15}(Me_3SiO_{1/2})_{0.05}(PhSiO_{3/2})_{0.5}(SiO_{4/2})_{0.2}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.3}(PhSiO_{3/2})_{0.7}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.4}(MeSiO_{3/2})_{0.6}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.5}(Me_2SiO_{2/2})_{0.5}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.6}(Me_2SiO_{2/2})_{0.4}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.7}(Me_2SiO_{2/2})_{0.3}$ ,  $(O_{3/2}SiSiMe_2O_{1/2})_{0.75}(PhSiO_{3/2})_{0.25}$ ,  $(O_{3/2}SiSiMeO_{2/2})_{0.75}(SiO_{4/2})_{0.25}$ ,  $(O_{2/2}MeSiSiMe_2O_{1/2})_{0.5}(O_{2/2}MeSiSiO_{3/2})_{0.3}(PhSiO_{3/2})_{0.2}$ ,  $(O_{2/2}EtSiSiMeO_{2/2})_{0.8}(MeSiO_{3/2})_{0.05}(SiO_{4/2})_{0.15}$ ,  $(O_{2/2}MeSiSiO_{3/2})_{0.8}(Me_3SiO_{1/2})_{0.05}(Me_2SiO_{2/2})_{0.1}(SiO_{4/2})_{0.5}$ ,  $(O_{2/2}MeSiSiEtO_{2/2})_{0.25}(O_{3/2}SiSiMeO_{2/2})_{0.6}(MeSiO_{3/2})_{0.1}(SiO_{4/2})_{0.05}$ ,  $(O_{1/2}Me_2SiSiMeO_{2/2})_{0.75}(O_{2/2}MeSiSiMeO_{2/2})_{0.25}$ ,  $(O_{1/2}Et_2SiSiEtO_{2/2})_{0.5}(O_{2/2}EtSiSiEtO_{2/2})_{0.5}$ ,  $(O_{1/2}Et_2SiSiEtO_{2/2})_{0.2}(O_{2/2}MeSiSiMeO_{2/2})_{0.8}$ , and  $(O_{1/2}Me_2SiSiMeO_{2/2})_{0.6}(O_{2/2}EtSiSiEtO_{2/2})_{0.4}$ , where Me is methyl, Et is ethyl, Ph is phenyl, the resin contains siloxane units in the form of particles, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

**[0101]** The silicone resin of the second embodiment can be prepared by (i) reacting at least one halodisilane having the formula  $Z_{3-a}R^1_aSi-SiR^1_bZ_{3-b}$  and, optionally, at least one halosilane having the formula  $R^1_bSiZ_{4-b}$  with at least one alcohol having the formula  $R^4OH$

in the presence of an organic solvent to produce an alcoholysis product, wherein each  $R^1$  is independently  $-H$ , hydrocarbyl, or substituted hydrocarbyl,  $R^4$  is alkyl or cycloalkyl,  $Z$  is halo,  $a = 0, 1, \text{ or } 2$ , and  $b = 0, 1, 2 \text{ or } 3$ ; (ii) reacting the alcoholysis product with water in the presence of siloxane particles at a temperature of from  $0$  to  $40$  °C to produce a hydrolyzate; and (iii) heating the hydrolyzate to produce the resin.

**[0102]** Step (i) of the method of preparing the silicone resin of the second embodiment is as described above for step (i) of the method of preparing the silicone resin of the first embodiment.

**[0103]** In step (ii) of the method of preparing the silicone resin of the second embodiment, the alcoholysis product is reacted with water in the presence of siloxane particles at a temperature of from  $0$  to  $40$  °C to produce a hydrolyzate.

**[0104]** The siloxane particles of the present method can be any particles comprising siloxane units. The siloxane units may be represented by the following formulae:

$R^1_2SiO_{1/2}$  units (M units),  $R^1_2SiO_{2/2}$  units (D units),  $R^1SiO_{3/2}$  units (T units), and  $SiO_{4/2}$  units (Q units), where  $R^1$  is as described and exemplified above.

**[0105]** The siloxane particles typically have a median particle size (based on mass) of from  $0.001$  to  $500$   $\mu\text{m}$ , alternatively from  $0.01$  to  $100$   $\mu\text{m}$ .

**[0106]** Although the shape of the siloxane particles is not critical, particles having a spherical shape are preferred because they generally impart a smaller increase in viscosity to the silicone composition than particles having other shapes.

**[0107]** Examples of siloxane particles include, but are not limited to, silica particles comprising  $SiO_{4/2}$  units, such as colloidal silica, dispersed pyrogenic (fumed) silica, precipitated silica, and coacervated silica; silicone resin particles comprising  $R^1SiO_{3/2}$  units, such as particles comprising  $MeSiO_{3/2}$  units, particles comprising  $MeSiO_{3/2}$  units and  $PhSiO_{3/2}$  units, and particles comprising  $MeSiO_{3/2}$  units and  $Me_2SiO_{2/2}$  units; and silicone elastomer particles comprising  $R^1_2SiO_{2/2}$  units, such as particles comprising a cross-linked product of a poly(dimethylsiloxane/methylvinylsiloxane) and a poly(hydrogen-methylsiloxane/dimethylsiloxane); wherein  $R^1$  is as described and exemplified above.

**[0108]** The siloxane particles can also be a metal polysilicate having the formula  $(M^{+a}O_{a/2})_x(SiO_{4/2})_y$ , where  $M$  is a metal cation having the charge  $+a$ , where  $a$  is an integer from  $1$  to  $7$ ,  $x$  has a value of from greater than zero to  $0.01$ ,  $y$  has a value of from  $0.99$  to less

than 1, and the sum  $x+y=1$ . Examples of metals include, but are not limited to, alkali metals such as sodium and potassium; alkaline earth metals such as beryllium, magnesium, and calcium; transition metals such as iron, zinc, chromium, and zirconium; and aluminum. Examples of metal polysilicates include a polysilicate having the formula  $(\text{Na}_2\text{O})_{0.01}(\text{SiO}_2)_{0.99}$ .

**[0109]** The siloxane particles can also be treated siloxane particles prepared by treating the surfaces of the aforementioned particles with an organosilicon compound. The organosilicon compound can be any of the organosilicon compounds typically used to treat silica fillers. Examples of organosilicon compounds include, but are not limited to, organochlorosilanes such as methyltrichlorosilane, dimethyldichlorosilane, and trimethyl monochlorosilane; organosiloxanes such as hydroxy-endblocked dimethylsiloxane oligomer, hexamethyldisiloxane, and tetramethyldivinyldisiloxane; organosilazanes such as hexamethyldisilazane, hexamethylcyclotrisilazane; and organoalkoxysilanes such as methyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and 3-methacryloxypropyltrimethoxysilane.

**[0110]** The siloxane particles of the present method can comprise a single type of siloxane particles or two or more different types of siloxane particles that differ in at least one of the following properties: composition, surface area, surface treatment, particle size, and particle shape.

**[0111]** Methods of preparing silicone resin particles and silicone elastomer particles are well known in the art. For example, silicone resin particles can be prepared by the hydrolysis-condensation of alkoxysilane(s) in an aqueous alkaline medium, as exemplified in U.S. Patent No. 5,801,262 and U.S. Patent No. 6,376,078. Silicone elastomer particles can be prepared by spray drying and curing a curable organopolysiloxane composition, as described in Japanese Patent Application No. 59096122; spray-drying an aqueous emulsion of a curable organopolysiloxane composition, as disclosed in U.S. Patent No. 4,761,454; curing an emulsion of a liquid silicone rubber microsuspension, as disclosed in U.S. Patent No. 5,371,139; or pulverizing cross-linked silicone rubber elastomer.

**[0112]** The alcoholysis product is typically combined with water by adding the alcoholysis product to a mixture of the water and siloxane particles. Reverse addition, i.e., addition of water to the alcoholysis product is also possible. However, reverse addition may result in formation of predominately gels.

[0113] The rate of addition of the alcoholysis product to the mixture of water and siloxane particles is typically from 2 mL/min. to 100 mL/min. for a 1000-mL reaction vessel equipped with an efficient means of stirring. When the rate of addition is too slow, the reaction time is unnecessarily prolonged. When the rate of addition is too fast, the reaction mixture may form a gel.

[0114] The reaction temperature, reaction time, and concentration of water in the reaction mixture are as described above for step (ii) of the method of preparing the silicone resin of the first embodiment.

[0115] The concentration of the siloxane particles in the reaction mixture is typically from 0.0001 to 99% (w/w), alternatively from 1 to 80 % (w/w), alternatively from 10 to 50% (w/w), based on the total weight of the reaction mixture.

[0116] Step (iii) of the method of preparing the silicone resin of the second embodiment is as described above for step (iii) of the method of preparing the silicone resin of the first embodiment. Furthermore, the silicone resin of the second embodiment can be recovered from the reaction mixture as described above for the silicone resin of the first embodiment.

[0117] Component (A) of the curable silicone composition can comprise a single silicone resin or a mixture comprising two or more different silicone resins, each as described above.

[0118] The concentration of component (A) is typically from 0.01 to 99.99% (w/w), alternatively from 20 to 99% (w/w), alternatively from 30 to 95% (w/w), alternatively from 50 to 80% (w/w), based on the total weight of the curable silicone composition.

[0119] Component (B) of the silicone composition is at least one organic solvent. The organic solvent can be any protic, aprotic, or dipolar aprotic organic solvent that does not react with the silicone resin or any optional ingredients (e.g., a crosslinking agent) and is miscible with the silicone resin.

[0120] Examples of organic solvents include, but are not limited to, alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-butanol, 1-pentanol, and cyclohexanol; saturated aliphatic hydrocarbons such as n-pentane, hexane, n-heptane, isooctane and dodecane; cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene and mesitylene; cyclic ethers such as tetrahydrofuran (THF) and dioxane; ketones such as methyl isobutyl ketone (MIBK); halogenated alkanes such as trichloroethane; and halogenated aromatic hydrocarbons such as bromobenzene and chlorobenzene. Component (B) can be a single

organic solvent or a mixture comprising two or more different organic solvents, each as defined above.

**[0121]** The concentration of component (B) is typically from 0.01% to 99.9% by weight, alternatively from 40 to 95% by weight, alternatively from 60% to 90% by weight, based on the total weight of the curable silicone composition.

**[0122]** The curable silicone composition can comprise additional ingredients, provided the ingredient does not prevent the silicone resin from forming a cured silicone resin, as described below. Examples of additional ingredients include, but are not limited to, adhesion promoters; dyes; pigments; anti-oxidants; heat stabilizers; UV stabilizers, flame retardants, flow control additives, cross-linking agents, and condensation catalysts.

**[0123]** The curable silicone composition can further comprises a cross-linking agent and/or a condensation catalyst. The cross-linking agent can have the formula  $R^3_qSiX_{4-q}$ , wherein  $R^3$  is  $C_1$  to  $C_8$  hydrocarbyl, X is a hydrolysable group, and q is 0 or 1. The hydrocarbyl groups represented by  $R^3$  are as described and exemplified above.

**[0124]** As used herein the term "hydrolysable group" means the silicon-bonded group reacts with water in the absence of a catalyst at any temperature from room temperature ( $\sim 23 \pm 2$  °C) to 100 °C within several minutes, for example thirty minutes, to form a silanol (Si-OH) group. Examples of hydrolysable groups represented by X include, but are not limited to, -Cl, -Br,  $-OR^3$ ,  $-OCH_2CH_2OR^4$ ,  $CH_3C(=O)O-$ ,  $Et(Me)C=N-O-$ ,  $CH_3C(=O)N(CH_3)-$ , and  $-ONH_2$ , wherein  $R^3$  and  $R^4$  are as described and exemplified above.

**[0125]** Examples of cross-linking agents include, but are not limited to, alkoxy silanes such as  $MeSi(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_3)_3$ ,  $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_3Si[O(CH_2)_3CH_3]_3$ ,  $CH_3CH_2Si(OCH_2CH_3)_3$ ,  $C_6H_5Si(OCH_3)_3$ ,  $C_6H_5CH_2Si(OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_3)_3$ ,  $CH_2=CHSi(OCH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_3)_3$ ,  $CF_3CH_2CH_2Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_2OCH_3)_3$ ,  $CF_3CH_2CH_2Si(OCH_2CH_2OCH_3)_3$ ,  $CH_2=CHSi(OCH_2CH_2OCH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_2OCH_3)_3$ ,  $Si(OCH_3)_4$ ,  $Si(OC_2H_5)_4$ , and  $Si(OC_3H_7)_4$ ; organoacetoxysilanes such as  $CH_3Si(OCOCH_3)_3$ ,  $CH_3CH_2Si(OCOCH_3)_3$ , and  $CH_2=CHSi(OCOCH_3)_3$ ; organoiminoxysilanes such as  $CH_3Si[O-N=C(CH_3)CH_2CH_3]_3$ ,  $Si[O-N=C(CH_3)CH_2CH_3]_4$ , and  $CH_2=CHSi[O-N=C(CH_3)CH_2CH_3]_3$ ;

organoacetamidossilanes such as  $\text{CH}_3\text{Si}[\text{NHC}(=\text{O})\text{CH}_3]_3$  and  $\text{C}_6\text{H}_5\text{Si}[\text{NHC}(=\text{O})\text{CH}_3]_3$ ; amino silanes such as  $\text{CH}_3\text{Si}[\text{NH}(\text{s-C}_4\text{H}_9)]_3$  and  $\text{CH}_3\text{Si}(\text{NHC}_6\text{H}_{11})_3$ ; and organoaminooxysilanes.

**[0126]** The cross-linking agent can be a single silane or a mixture of two or more different silanes, each as described above. Also, methods of preparing tri- and tetra-functional silanes are well known in the art; many of these silanes are commercially available.

**[0127]** When present, the concentration of the cross-linking agent in the silicone composition is sufficient to cure (cross-link) the silicone resin. The exact amount of the cross-linking agent depends on the desired extent of cure, which generally increases as the ratio of the number of moles of silicon-bonded hydrolysable groups in the cross-linking agent to the number of moles of silicon-bonded hydroxy groups in the silicone resin increases. Typically, the concentration of the cross-linking agent is sufficient to provide from 0.2 to 4 moles of silicon-bonded hydrolysable groups per mole of silicon-bonded hydroxy groups in the silicone resin. The optimum amount of the cross-linking agent can be readily determined by routine experimentation.

**[0128]** As stated above, the silicone composition can further comprise at least one condensation catalyst. The condensation catalyst can be any condensation catalyst typically used to promote condensation of silicon-bonded hydroxy (silanol) groups to form Si-O-Si linkages. Examples of condensation catalysts include, but are not limited to, amines; and complexes of lead, tin, zinc, and iron with carboxylic acids. In particular, the condensation catalyst can be selected from tin(II) and tin(IV) compounds such as tin dilaurate, tin dioctoate, and tetrabutyl tin; and titanium compounds such as titanium tetrabutoxide.

**[0129]** The concentration of the condensation catalyst is typically from 0.1 to 10% (w/w), alternatively from 0.5 to 5% (w/w), alternatively from 1 to 3% (w/w), based on the total weight of the silicone resin.

**[0130]** When the silicone composition described above contains a condensation catalyst, the composition is typically a two-part composition where the silicone resin and condensation catalyst are in separate parts.

**[0131]** The curable composition comprising a thermosetting polymer can further comprise a carbon nanomaterial, which is as described and exemplified above. When present, the carbon nanomaterial typically has a concentration of from 0.0001 to 99% (w/w), alternatively from 0.001 to 50% (w/w), alternatively from 0.01 to 25% (w/w), alternatively from 0.1 to 10%

(w/w), alternatively from 1 to 5% (w/w), based on the total weight of the thermosetting polymer.

**[0132]** The release liner can be coated with the curable composition comprising a thermosetting polymer using conventional coating techniques, such as spin coating, dipping, spraying, brushing, extrusion, or screen-printing. The amount of the composition is sufficient to form a first polymer layer having a thickness of from 0.01 to 1000  $\mu\text{m}$  after the polymer is cured in step (ii) of the method, described below.

**[0133]** In step (ii) of the immediately preceding method of forming the first polymer layer, the thermosetting polymer of the coated release liner is cured. The thermosetting polymer can be cured using a variety of methods, including exposing the polymer to ambient temperature, elevated temperature, moisture, or radiation, depending on the type of curable composition used to coat the release liner.

**[0134]** When the curable composition used to coat the release liner is a curable silicone composition comprising (A) at least one silicone resin comprising disilyloxane units having the formula (I) and (B) an organic solvent, the silicone resin of the coated release liner can be cured by heating the coating at a temperature sufficient to cure the silicone resin. For example, the silicone resin can typically be cured by heating the coating at a temperature of from 50 to 250  $^{\circ}\text{C}$ , for a period of from 1 to 50 h. When the condensation-curable silicone composition comprises a condensation catalyst, the silicone resin can typically be cured at a lower temperature, e.g., from room temperature ( $\sim 23 \pm 2$   $^{\circ}\text{C}$ ) to 200  $^{\circ}\text{C}$ .

**[0135]** The silicone resin can be cured at atmospheric or subatmospheric pressure. For example, when the coating is not enclosed between two release liners, the silicone resin is typically cured at atmospheric pressure in air. Alternatively, when the coating is enclosed between a first and second release liner, described below, the silicone resin is typically cured under reduced pressure. For example, the silicone resin can be heated under a pressure of from 1,000 to 20,000 Pa, alternatively from 1,000 to 5,000 Pa. The silicone resin can be cured under reduced pressure using a conventional vacuum bagging process. In a typically process, a bleeder (e.g., polyester) is applied over the coated release liner, a breather (e.g., Nylon, polyester) is applied over the bleeder, a vacuum bagging film (e.g., Nylon) equipped with a vacuum nozzle is applied over the breather, the assembly is sealed with tape, a vacuum (e.g., 1,000 Pa) is applied to the sealed assembly and, if necessary, the evacuated assembly is heated as described above.

**[0136]** The method of forming the first polymer layer, wherein the layer comprises a thermoset polymer, can further comprise, after step (i) and before step (ii), applying a second release liner to the coated release liner of the first step to form an assembly, and compressing the assembly. The assembly can be compressed to remove excess composition and/or entrapped air, and to reduce the thickness of the coating. The assembly can be compressed using conventional equipment such as a stainless steel roller, hydraulic press, rubber roller, or laminating roll set. The assembly is typically compressed at a pressure of from 1,000 Pa to 10 MPa and at a temperature of from room temperature ( $\sim 23 \pm 2$  °C) to 50 °C.

**[0137]** The method of forming the first polymer layer, wherein the layer comprises a thermoset polymer, can further comprise repeating the steps (i) and (ii) to increase the thickness of the polymer layer, provided the same curable composition is used for each coating step.

**[0138]** When the first polymer layer comprises a thermoplastic polymer and a fiber reinforcement, the polymer layer can be formed by (a) impregnating a fiber reinforcement in a composition comprising a thermoplastic polymer in a fluid state and (b) converting the thermoplastic polymer of the impregnated fiber reinforcement to a solid state.

**[0139]** In step (a) of the immediately preceding method of forming the first polymer layer, a fiber reinforcement is impregnated in a composition comprising a thermoplastic polymer in a fluid state.

**[0140]** The fiber reinforcement can be impregnated in a composition comprising a thermoplastic polymer in a fluid state using a variety of methods. For example, according to a first method, the fiber reinforcement can be impregnated by (i) applying a composition comprising a thermoplastic polymer in a fluid state to a release liner to form a film; (ii) embedding a fiber reinforcement in the film; and (iii) applying the composition to the embedded fiber reinforcement to form an impregnated fiber reinforcement.

**[0141]** In step (i) of the immediately preceding method of impregnating a fiber reinforcement, a composition comprising a thermoplastic polymer in a fluid state is applied to a release liner to form a film. The release liner and the composition are as described and exemplified above. The composition can be applied to the release liner using conventional coating techniques, such as spin coating, dipping, spraying, brushing, extrusion, or screen-printing. The composition is applied in an amount sufficient to embed the fiber reinforcement in step (ii), below.

[0142] In step (ii), a fiber reinforcement is embedded in the film. The fiber reinforcement is as described and exemplified above. The fiber reinforcement can be embedded in the film by simply placing the reinforcement on the film and allowing the composition of the film to saturate the reinforcement.

[0143] In step (iii) the composition comprising a thermoplastic polymer in a fluid state is applied to the embedded fiber reinforcement to form an impregnated fiber reinforcement. The composition can be applied to the embedded fiber reinforcement using conventional methods, as described above for step (i).

[0144] The first method of impregnating a fiber reinforcement can further comprise the steps of (iv) applying a second release liner to the impregnated fiber reinforcement to form an assembly; and (v) compressing the assembly. Also, the first method can further comprise after step (ii) and before step (iii), degassing the embedded fiber reinforcement and/or after step (iii) and before step (iv), degassing the impregnated fiber reinforcement.

[0145] The assembly can be compressed to remove excess composition and/or entrapped air, and to reduce the thickness of the impregnated fiber reinforcement. The assembly can be compressed using conventional equipment such as a stainless steel roller, hydraulic press, rubber roller, or laminating roll set. The assembly is typically compressed at a pressure of from 1,000 Pa to 10 MPa and at a temperature of from room temperature to 200 °C.

[0146] The embedded fiber reinforcement or impregnated fiber reinforcement can be degassed by subjecting it to a vacuum at a temperature sufficient to maintain the fluid state of the thermoplastic polymer.

[0147] Alternatively, according to a second method, the fiber reinforcement can be impregnated in the composition comprising a thermoplastic polymer in a fluid state by (i) depositing a fiber reinforcement on a release liner; (ii) embedding the fiber reinforcement in a composition comprising a thermoplastic polymer in a fluid state; and (iii) applying the composition to the embedded fiber reinforcement to form an impregnated fiber reinforcement. The second method can further comprise the steps of (iv) applying a second release liner to the impregnated fiber reinforcement to form an assembly; and (v) compressing the assembly. In the second method, steps (iii) to (v) are as described above for the first method of impregnating a fiber reinforcement in a composition comprising a thermoplastic polymer in a fluid state. Also, the second method can further comprise after

step (ii) and before step (iii), degassing the embedded fiber reinforcement and/or after step (iii) and before step (iv), degassing the impregnated fiber reinforcement.

**[0148]** In step (ii) of the immediately preceding method of impregnating a fiber reinforcement, a fiber reinforcement is embedded in a composition comprising a thermoplastic polymer in a fluid state. The fiber reinforcement can be embedded in the composition by simply covering the reinforcement with the composition and allowing the composition to saturate the reinforcement.

**[0149]** Furthermore, when the fiber reinforcement is a woven or nonwoven fabric, the reinforcement can be impregnated in a composition comprising a thermoplastic polymer in a fluid state by passing it through the composition. The fabric is typically passed through the composition at a rate of from 1 to 1,000 cm/min.

**[0150]** In step (b) of the preceding method of forming the first polymer layer, the thermoplastic polymer of the impregnated fiber reinforcement is converted to a solid state. When the composition used to coat the release liner comprises a thermoplastic polymer in a molten state, the thermoplastic polymer can be converted to a solid state by allowing the polymer to cool to a temperature below the liquid-solid transition temperature ( $T_g$  or  $T_m$ ), for example, room temperature. When the composition used to coat the release liner comprises a thermoplastic polymer and an organic solvent, the thermoplastic polymer can be converted to a solid state by removing at least a portion of the solvent. The organic solvent can be removed by allowing the solvent to evaporate at ambient temperature or by heating the coating to a moderate temperature, for example, below the solid-liquid transition temperature of the polymer.

**[0151]** The method of forming the first polymer layer, wherein the layer contains a composition comprising a thermoplastic resin in fluid state and a fiber reinforcement, can further comprise repeating the steps (a) and (b) to increase the thickness of the polymer layer, provided the same composition is used for each impregnation.

**[0152]** When the first polymer layer comprises a thermoset polymer and a fiber reinforcement, the polymer layer can be formed by (a') impregnating a fiber reinforcement in a curable composition comprising a thermosetting polymer; and (b') curing the thermosetting polymer of the impregnated fiber reinforcement.

**[0153]** In step (a') of the immediately preceding method of forming the first polymer layer, a fiber reinforcement is impregnated in a curable composition comprising a thermosetting

polymer. The fiber reinforcement and composition are as described and exemplified above. The fiber reinforcement can be impregnated in the curable composition using the method described above for impregnating a fiber reinforcement in a composition comprising a thermoplastic polymer.

**[0154]** In step (b') of the immediately preceding method of forming the first polymer layer, the thermosetting polymer of the impregnated fiber reinforcement is cured. The thermosetting polymer can be cured using a variety of methods, including, exposing the impregnated fiber reinforcement to ambient or elevated temperature, moisture, or radiation, depending on the type of curable composition used to impregnate the fiber reinforcement.

**[0155]** When the curable composition used to impregnate the fiber reinforcement is a curable silicone composition comprising (A) at least one silicone resin comprising disilyloxane units having the formula (I) and (B) an organic solvent, the silicone resin can be cured by heating the impregnated fiber reinforcement at a temperature sufficient to cure the silicone resin. For example, the silicone resin can typically be cured by heating the impregnated fiber reinforcement at a temperature of from 50 to 250 °C, for a period of from 1 to 50 h. When the condensation-curable silicone composition comprises a condensation catalyst, the silicone resin can typically be cured at a lower temperature, e.g., from room temperature ( $\sim 23 \pm 2$  °C) to 200 °C.

**[0156]** The silicone resin of the impregnated fiber reinforcement can be cured at atmospheric or subatmospheric pressure, depending on the method, described above employed to impregnate the fiber reinforcement in the condensation-curable silicone composition. For example, when the coating is not enclosed between two release liners, the silicone resin is typically cured at atmospheric pressure in air. Alternatively, when the coating is enclosed between a first and second release liner, the silicone resin is typically cured under reduced pressure. For example, the silicone resin can be heated under a pressure of from 1,000 to 20,000 Pa, alternatively from 1,000 to 5,000 Pa. The silicone resin can be cured under reduced pressure using a conventional vacuum bagging process. In a typically process, a bleeder (e.g., polyester) is applied over the coated release liner, a breather (e.g., Nylon, polyester) is applied over the bleeder, a vacuum bagging film (e.g., Nylon) equipped with a vacuum nozzle is applied over the breather, the assembly is sealed with tape, a vacuum (e.g., 1,000 Pa) is applied to the sealed assembly and, if necessary, the evacuated assembly is heated as described above.

**[0157]** The method of preparing the first polymer layer, wherein the layer comprises a thermoset polymer and a fiber reinforcement, can further comprise repeating the steps (a') and (b') to increase the thickness of the polymer layer, provided the same curable composition is used for each impregnation.

**[0158]** In the second step of the method of preparing the reinforced silicone resin film, at least one additional polymer layer is formed on the first polymer layer. Each additional polymer layer can be formed as described above in the method of forming the first polymer layer, except each additional polymer layer is formed directly on an existing polymer layer rather than a release liner.

**[0159]** When the first polymer layer is formed on a release liner, the method of preparing the reinforced silicone resin film further comprises separating the first polymer layer from the release liner. The first polymer layer can be separated from the release liner either before or after at least one additional polymer layer is formed. Moreover, the first polymer layer can be separated from the release liner by mechanically peeling the layer away from the release liner. When the first polymer layer is formed between two release liners, the method of preparing the reinforced silicone resin film further comprises separating the first polymer layer from at least one of the release liners before at least one additional polymer layer is formed on the first polymer layer.

**[0160]** The reinforced silicone resin films of the present invention typically comprise from 1 to 99% (w/w), alternatively from 10 to 95% (w/w), alternatively from 30 to 95% (w/w), alternatively from 50 to 95% (w/w), of the cured silicone resin. Also, the reinforced silicone resin films typically have a thickness of from 1 to 3000  $\mu\text{m}$ , alternatively from 15 to 500  $\mu\text{m}$ , alternatively from 15 to 300  $\mu\text{m}$ , alternatively from 20 to 150  $\mu\text{m}$ , alternatively from 30 to 125  $\mu\text{m}$ .

**[0161]** The reinforced silicone resin films typically have a flexibility such that the films can be bent over a cylindrical steel mandrel having a diameter less than or equal to 3.2 mm without cracking, where the flexibility is determined as described in ASTM Standard D522-93a, Method B.

**[0162]** The reinforced silicone resin films have low coefficient of linear thermal expansion (CTE), high tensile strength, high modulus, and high resistance to thermally induced cracking. For example the films typically have a CTE of from 0 to 80  $\mu\text{m}/\text{m}^\circ\text{C}$ , alternatively from 0 to 20  $\mu\text{m}/\text{m}^\circ\text{C}$ , alternatively from 2 to 10  $\mu\text{m}/\text{m}^\circ\text{C}$ , at temperature of from room

temperature ( $\sim 23 \pm 2$  °C) to 200°C. Also, the films typically have a tensile strength at 25 °C of from 5 to 200 MPa, alternatively from 20 to 200 MPa, alternatively from 50 to 200 MPa. Further, the reinforced silicone resin films typically have a Young's modulus at 25 °C of from 0.5 to 10 GPa, alternatively from 1 to 6 GPa, alternatively from 3 to 5 GPa.

**[0163]** The transparency of the reinforced silicone resin films depends on a number of factors, such as the composition of the cured silicone resin, the thickness of the film, and the type and concentration of the reinforcement. The reinforced silicone resin films typically have a transparency (% transmittance) of at least 5%, alternatively at least 10%, alternatively at least 15%, alternatively at least 20%, in the visible region of the electromagnetic spectrum.

**[0164]** The reinforced silicone resin films of the present invention are useful in applications requiring films having high thermal stability, flexibility, mechanical strength, and transparency. For example, the silicone resin films can be used as integral components of flexible displays, solar cells, flexible electronic boards, touch screens, fire-resistant wallpaper, and impact-resistant windows. The films are also suitable substrates for transparent or nontransparent electrodes.

## EXAMPLES

**[0165]** The following examples are presented to better illustrate the reinforced silicone resin film and method of the present invention, but are not to be considered as limiting the invention, which is delineated in the appended claims. Unless otherwise noted, all parts and percentages reported in the examples are by weight. The following materials were employed in the examples:

**[0166]** Pyrograf<sup>®</sup>-III grade HHT-19 carbon nanofiber, sold by Pyrograf Products, Inc. (Cedarville, Ohio), is a heat-treated (up to 3000 °C) carbon nanofiber having a diameter of 100 to 200 nm and a length of 30,000 to 100,000 nm.

**[0167]** Disilane Composition A is a chlorodisilane stream obtained by fractional distillation of the residue produced in the direct process for manufacturing methylchlorosilanes. The composition contains Me<sub>4</sub>Cl<sub>2</sub>Si<sub>2</sub>, 1.63%; Me<sub>3</sub>Cl<sub>3</sub>Si<sub>2</sub>, 33.7%, and Me<sub>2</sub>Cl<sub>4</sub>Si<sub>2</sub>, 63.75%, based on total weight.

**[0168]** SDC MP101 Crystal Coat Resin, which is sold by SDC Technologies, Inc. (Anaheim, CA) is a solution containing 31% (w/w) of a silicone resin consisting essentially

of  $\text{MeSiO}_{3/2}$  units and  $\text{SiO}_{4/2}$  units in a mixture of methanol, 2-propanol, water, and acetic acid (~1-2%).

**[0169]** Glass Fabric is a heat-treated glass fabric prepared by heating style 106 electrical glass fabric having a plain weave and a thickness of 37.5  $\mu\text{m}$  at 575 °C for 6 h. The untreated glass fabric was obtained from JPS Glass (Slater, SC).

#### Example 1

**[0170]** This example demonstrates the preparation of a chemically oxidized carbon nanofiber. Pyrograf<sup>®</sup>-III carbon nanofiber ( 2.0 g), 12.5 mL of concentrated nitric acid, and 37.5 mL of concentrated sulfuric acid were combined sequentially in a 500-mL three-neck flask equipped with a condenser, a thermometer, a Teflon-coated magnetic stirring bar, and a temperature controller. The mixture was heated to 80 °C and kept at this temperature for 3 h. The mixture was then cooled by placing the flask on a layer of dry ice in a one gallon pail. The mixture was poured into a Buchner funnel containing a nylon membrane (0.8  $\mu\text{m}$ ) and the carbon nanofibers were collected by vacuum filtration. The nanofibers remaining on the membrane were washed several times with deionized water until the pH of the filtrate was equal to the pH of the wash water. After the last wash, the carbon nanofibers were kept in the funnel for an additional 15 min. with continued application of the vacuum. Then the nanofibers, supported on the filter membrane, were placed in an oven at 100 °C for 1 h. The carbon nanofibers were removed from filter membrane and stored in a dry sealed glass jar.

#### Example 2

**[0171]** Disilane Composition A (15 g), was mixed with 28.6 g  $\text{PhSiCl}_3$ , 120 g of methyl isobutyl ketone, and 19.48 g of anhydrous methanol. The HCl produced from the reaction was allowed to escape from the open mouth of the flask. The liquid mixture was placed in a sealed bottle, chilled in an ice water bath, and then transferred to an addition funnel mounted on top of a three necked round bottom flask equipped with a stirrer and a thermometer. Deionized water (120 g) was placed in the flask and cooled with an external ice water bath to 2 to 4 °C. The mixture in the addition funnel was continuously added to the chilled deionized water over a period of 10 min., during which time the temperature of the mixture increased by 3 to 5 °C. After completion of the addition, the mixture was stirred in the ice bath for 1 h.

The flask was then heated to 50 to 75 °C with a water bath and held at that temperature for 1 h. The mixture was allowed to cool to room temperature and then washed with a solution of 10 g of NaCl in 200 mL of water, four times. After each wash the aqueous phase was discarded. The organic phase was isolated, centrifuged, and filtered. The organic phase had a silicone resin content of 21.25% (w/w).

#### Example 3

**[0172]** The oxidized carbon nanofiber of Example 1 (0.011 g) and 26 g of the silicone resin preparation of Example 2 were combined in a glass vial. The vial was placed in an ultrasonic bath for 30 min. The mixture was then subjected to centrifugation at 2000 rpm for 30 min. The supernatant silicone composition was used to prepare reinforced silicone resin films, as described below.

#### Example 4

**[0173]** Glass fabric (38.1 cm x 8.9 cm) was impregnated with the silicone composition of Example 3 by passing the fabric through the composition at a rate of about 5 cm/s. The impregnated fabric was hung vertically in a fume hood at room temperature for 2 h, and then cured in an air-circulating oven according to the following cycle: 50 °C, 2 h; 50 °C to 150 °C at 2.5 °C/min., 150 °C for 0.5h. The oven was turned off and the reinforced silicone resin film was allowed to cool to room temperature.

**[0174]** The film was then impregnated with a silicone composition prepared by diluting MP101 Crystal Coat Resin to 10.35% (w/w) resin with 2-propanol. The impregnated fabric was hung vertically in a fume hood at room temperature over night, and then cured in an air-circulating oven according to the following cycle: room temperature to 75 °C at 1 °C/min., 75 °C for 1 h; 75 °C to 100 °C at 1 °C/min., 100 °C for 1 h; 100 °C to 125 °C at 1 °C/min., 125 °C for 1 h. The mechanical properties of the three-layer reinforced silicone resin film are shown in Table 1.

#### Example 5

**[0175]** Disilane Composition A (50 g), was mixed with 31 g MeSiCl<sub>3</sub>, 300 g of methyl isobutyl ketone, and 80 ml of anhydrous methanol. The HCl produced from the reaction was allowed to escape from the open mouth of the flask. The liquid mixture was placed in a

sealed bottle, chilled in an ice water bath, and then transferred to an addition funnel mounted on top of a three necked round bottom flask equipped with a stirrer and a thermometer. Deionized water (250 g) was placed in the flask and cooled with an external ice water bath to 2 to 4 °C. The mixture in the addition funnel was continuously added to the chilled deionized water over a period of 10 min., during which time the temperature of the mixture increased by 3 to 5 °C. After completion of the addition, the mixture was stirred in the ice bath for 1 h. The flask was then heated to 50 to 75 °C with a water bath and held at that temperature for 1 h. The mixture was allowed to cool to room temperature and then washed with a solution of 10 g of NaCl in 200 mL of water, four times. After each wash the aqueous phase was discarded. The organic phase was isolated, centrifuged, and filtered. The organic phase had a silicone resin content of 13.70% (w/w). The organic phase was then concentrated at 80 °C and a pressure of 5 mm Hg (667 Pa) to produce a solution containing to 27.40% (w/w) of the silicone resin.

#### Example 6

[0176] The oxidized carbon nanofiber of Example 1 (0.011 g) and 26 g of the silicone resin preparation of Example 5 were combined in a glass vial. The vial was placed in an ultrasonic bath for 30 min. The mixture was then subjected to centrifugation at 2000 rpm for 30 min. The supernatant silicone composition was used to prepare reinforced silicone resin films, as described below.

#### Example 7

[0177] A reinforced silicone resin film was prepared according to the method of Example 4, except the silicone composition of Example 3 was replaced with the silicone composition of Example 6. The mechanical properties of the reinforced silicone resin film are shown in Table 1.

Table 1

Example	Thickness (mm)	Tensile Strength (MPa), Warp	Young's Modulus (GPa), Warp	Strain at Break (%), Warp
4	0.032	82.2	5.01	3.57
7	0.040	91.1	2.84	4.94

That which is claimed is:

1. A reinforced silicone resin film comprising at least two polymer layers, wherein at least one of the polymer layers comprises a cured product of at least one silicone resin comprising disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), wherein each  $R^1$  is independently  $-H$ , hydrocarbyl, or substituted hydrocarbyl,  $a$  is 0, 1, or 2, and  $b$  is 0, 1, 2 or 3; and at least one of the polymer layers comprises a carbon nanomaterial.
2. The reinforced silicone resin film according to claim 1, wherein each of the polymer layers has a thickness of from 0.01 to 1000  $\mu m$ .
3. The reinforced silicone resin film according to claim 1, wherein the film comprises from 1 to 10 polymer layers.
4. The reinforced silicone resin film according to claim 1, wherein the carbon nanomaterial is selected from at least one of carbon nanoparticles, fibrous carbon nanomaterials, and layered carbon nanomaterials.
5. The reinforced silicone resin film according to claim 4, wherein the carbon nanomaterial comprises carbon nanofibers.
6. The reinforced silicone resin film according to claim 1, wherein the carbon nanomaterial is an oxidized carbon nanomaterial.
7. The reinforced silicone resin film according to claim 1, wherein the concentration of the carbon nanomaterial in the polymer layer is from 0.001 to 50% (w/w), based on the total weight of the polymer layer.

8. The reinforced silicone resin film according to claim 1, wherein at least one of the polymer layers comprises a reinforcement selected from at least one of a carbon nanomaterial and a fiber reinforcement.

9. The reinforced silicone resin film according to claim 8, wherein the fiber reinforcement comprises glass fibers.

10. The reinforced silicone resin film according to claim 1, wherein the silicone resin comprises at least 5 mol% of disilyloxane units having the formula (I).

11. The reinforced silicone resin film according to claim 1, wherein the silicone resin comprises in addition to disilyloxane units having the formula (I), other siloxane units.

12. The reinforced silicone resin film according to claim 1, wherein the silicone resin has the formula:  $[O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}]_v(R^1_3SiO_{1/2})_w(R^1_2SiO_{2/2})_x(R^1SiO_{3/2})_y(SiO_{4/2})_z$  (II), wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl; a is 0, 1, or 2; b is 0, 1, 2 or 3; v is from 0.01 to 1; w is from 0 to 0.84; x is from 0 to 0.99; y is from 0 to 0.99; z is from 0 to 0.95; and  $v+w+x+y+z = 1$ .

13. The reinforced silicone resin film according to claim 1, wherein the the silicone resin comprises disilyloxane units having the formula  $O_{(3-a)/2}R^1_aSi-SiR^1_bO_{(3-b)/2}$  (I), and siloxane units having the form of particles, wherein each  $R^1$  is independently -H, hydrocarbyl, or substituted hydrocarbyl; a is 0, 1, or 2; and b is 0, 1, 2 or 3.

14. The reinforced silicone resin film according to claim 13, wherein the silicone resin comprises from 10 to 70 mol% of disilyloxane units having the formula (I).

15. The reinforced silicone resin film according to claim 13, wherein the silicone resin comprises in addition to disilyloxane units having the formula (I) and siloxane units having the form of particles, other siloxane units.

16. The reinforced silicone resin film according to claim 13, wherein the silicone resin comprises from 1 to 80 mol% of siloxane units having the form of particles.

17. The reinforced silicone resin film according to claim 13, wherein the particles have a median size of from 0.001 to 500  $\mu\text{m}$ .

18. The reinforced silicone resin film according to claim 13, wherein the particles are selected from silica particles, silicone resin particles, silicone elastomer particles, and metal polysilicate particles.