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(54) Title: METHOD OF MAKING A HOLLOW FIBER USING A CORE INCLUDING A MELTABLE OR SUBLIMABLE COMPOSITION

(57) Abstract: The present invention relates to hollow fibers. In some embodiments, the present invention provides a method of forming a hollow fiber. The method can include providing or obtaining a solid core including a core composition that includes about 50 wt% to about 100 wt% of a composition that is at least one of meltable and sublimable. The method can include coating the core with a curable composition. The method can include curing the curable composition. The method can include melting or subliming at least part of the core composition, to provide a hollow fiber. In some examples, the hollow fiber can be an organopolysiloxane hollow fiber. In various embodiments, the present invention provides a hollow fiber made by the method, an organopolysiloxane-coated core, or a core coated with a cured organopolysiloxane composition.



METHOD OF MAKING A HOLLOW FIBER USING A CORE INCLUDING A MELTABLE OR SUBLIMABLE COMPOSITION

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application
5 Serial No. 61/778,947, filed March 13, 2013, the disclosure of which is incorporated herein in its entirety by reference.

[0002] Hollow fibers can be made from a variety of materials and are useful for a wide range of applications. For example, hollow fiber membranes can be used to separate one or more components from liquid or gaseous mixtures. Hollow fiber membranes have a
10 high surface area to volume ratio, and are an efficient way to utilize membranes to perform separations. However, the synthesis, handling, and transport of hollow fibers can be difficult and expensive.

SUMMARY OF THE INVENTION

[0003] In various embodiments, the present invention provides a method of forming a
15 hollow fiber. The method includes providing or obtaining a substantially cylindrical solid core. The core includes a core composition. The core composition includes about 50 wt% to about 100 wt% of a composition that is at least one of meltable and sublimable. The method includes coating the core with a curable composition. The method includes curing the curable composition. The method includes melting or subliming at least part of the core
20 composition. The method includes removing at least part of the melted or sublimed part of the core composition. The method provides a hollow fiber.

[0004] In various embodiments, the present invention provides a method of forming a silicone hollow fiber. The method includes providing or obtaining a substantially cylindrical solid core. The core has a diameter of about 100 μm to about 500 μm . The core includes
25 at least one supporting fiber. The core includes a core composition coating the supporting fiber. The core composition includes about 50 wt% to about 100 wt% of a meltable or sublimable composition. The meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$. The method includes coating the core with a curable composition comprising an organopolysiloxane. The method
30 includes curing the curable composition. The method also includes melting or subliming at least part of the core composition. The method also includes removing at least part of the melted or sublimed part of the core composition. The method provides a silicone hollow fiber including walls with a thickness of about 10 μm to about 60 μm .

[0005] In various embodiments, the present invention provides a method of forming a
35 silicone hollow fiber. The method includes providing or obtaining a substantially cylindrical solid core. The core has a diameter of about 100 μm to about 500 μm . The core includes a core composition. The core composition includes about 50 wt% to about 100 wt% of a

composition that has a zero shear viscosity of about 100 cP or less at at least one temperature of 0° C to 60° C. The method includes coating the core with a curable composition comprising an organopolysiloxane. The method includes curing the curable composition. The method includes melting or subliming at least part of the core composition. The method includes removing at least part of the melted or sublimed part of the core composition. The method provides a silicone hollow fiber comprising walls with a thickness of about 10 μm to about 60 μm.

[0006] In various embodiments, the present invention provides an organopolysiloxane-coated core. The coated core includes a solid substantially cylindrical core. The core has a diameter of about 10 μm to about 2000 μm. The core includes a core composition. The core composition includes about 50 wt% to about 100 wt% of a meltable or sublimable composition. The meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 °C to about 60 °C. The coated core includes a curable composition coated on the core. The curable composition includes an organopolysiloxane.

[0007] In various embodiments, the present invention provides a core coated with a cured organopolysiloxane composition. The coated core includes a solid substantially cylindrical core. The core has a diameter of about 10 μm to about 2000 μm. The core includes a core composition including about 50 wt% to about 100 wt% of a meltable or sublimable composition. The meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 °C to about 60 °C. The coated core includes an at least partially cured curable composition coated on the core. The curable composition includes an organopolysiloxane and includes walls having a thickness of about 1 μm to about 200 μm.

[0008] In various embodiments, the present invention provides a method of separating components in a feed mixture. The method includes contacting a first side of a membrane with a feed gas or liquid mixture. The feed mixture includes at least a first component and a second component. The contacting produces a permeate mixture on a second side of the membrane and a retentate mixture on the first side of the membrane. The permeate mixture is enriched in the first component. The retentate mixture is depleted in the first component. The membrane includes a hollow fiber provided by a method including providing or obtaining a solid core. The solid core includes at least one supporting fiber and a core composition. The core composition coats the supporting fiber. The core composition is at least one of meltable and sublimable. The method includes coating the core with a curable composition. The method includes curing the curable composition. The method also includes melting or subliming at least part of the core composition, to provide the hollow fiber.

[0009] Various embodiments have certain advantages over other methods of forming hollow fibers, hollow fibers made using the method, polysiloxane-coated cores, cores coated with cured curable polysiloxane compositions, or methods of using the hollow fiber to separate a mixture, at least some of which are unexpected. In some examples, the present method can provide hollow fibers with greater efficiency, lower cost, or greater resilience to damage during synthesis, handling, or transport, as compared to other methods of making hollow fibers. In some examples, the present method can be used to generate a wider variety of hollow fibers than other methods, for example due to at least one of the core stabilizing the coating prior to curing, the range of temperatures at which the core composition can melt or sublime, or by avoiding dissolving solvents. Various embodiments can be a useful alternative or a more effective method than other processes for making hollow microfibers, such as hollow fibers that cannot conveniently be directly formed from a melt or solution.

[0010] For example, in some embodiments removing the core using melting or sublimation is easier and more efficient than removing the core using dissolution. In some examples, melting or sublimation can be faster or easier than dissolution since the entire core can be melted or sublimed at approximately the same time, whereas in some examples dissolution can only or can predominantly dissolve the ends of the core accessible via an opening of the hollow fiber, or can require time for water to pass through the membrane before dissolution can occur. In some embodiments, the method can result in a more complete removal of the core than other methods, such as methods that only rely on dissolution. In some embodiments, the method can result in less waste, such as when the melted or sublimed material is recycled for reuse. In some embodiments, the method can allow for greater versatility in the shape of the hollow fiber generated.

[0011] In some embodiments, the present method can provide hollow fibers at less expense or that have at least one of a more consistent diameter, a smaller diameter, as compared to hollow fibers generated using extrusion techniques. In some embodiments of the present invention, the core can be allowed to remain in the hollow fiber during handling, transport, or other activities, which can advantageously stabilize the hollow fiber and help to prevent collapse or other damage. Thus, in some examples, the present method can provide a hollow fiber that is less likely to collapse during synthesis, handling, transport, or other activities, as compared to hollow fibers generated using other techniques such as extrusion techniques. In some embodiments, the present method can provide a hollow fiber that is easier to handle and easier to transport as compared to hollow fibers generated using other techniques such as extrusion techniques.

[0012] In some examples, the present method can provide a hollow fiber using a core that is meltable or sublimable at more convenient temperatures than used in other methods of

making hollow fibers. In some embodiments, the present method uses a core that is more easily synthesized than other methods. In some examples, the present method can be used to generate a wider variety of hollow fibers than other methods, for example due to at least one of the stabilizing effect of the core and the melting or sublimation temperature of the core.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Reference will now be made in detail to certain embodiments of the disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0014] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1% to 5%” should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement “about X to Y” has the same meaning as “about X to about Y,” unless indicated otherwise. Likewise, the statement “about X, Y, or about Z” has the same meaning as “about X, about Y, or about Z,” unless indicated otherwise.

[0015] In this document, the terms “a,” “an,” or “the” are used to include one or more than one unless the context clearly dictates otherwise. The term “or” is used to refer to a nonexclusive “or” unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0016] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited. Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For

example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

5 [0017] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0018] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

10 [0019] The term “organic group” as used herein refers to but is not limited to any carbon-containing functional group. Examples include acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroarylalkyl, linear and/or branched groups such as alkyl groups, fully or partially halogen-substituted haloalkyl groups, alkenyl groups, alkynyl groups, acrylate and methacrylate functional groups; and other organic functional groups such as ether groups,
15 cyanate ester groups, ester groups, carboxylate salt groups, and masked isocyano groups.

[0020] The term “substituted” as used herein refers to an organic group as defined herein or molecule in which one or more bonds to a hydrogen atom contained therein are replaced by one or more bonds to a non-hydrogen atom. The term “functional group” or “substituent” as used herein refers to a group that can be or is substituted onto a molecule,
20 or onto an organic group. Examples of substituents or functional groups include, but are not limited to, any organic group, a halogen (e.g., F, Cl, Br, and I); a sulfur atom in groups such as thiol groups, alkyl and aryl sulfide groups, sulfoxide groups, sulfone groups, sulfonyl groups, and sulfonamide groups; a nitrogen atom in groups such as amines, hydroxylamines, nitriles, nitro groups, N-oxides, hydrazides, azides, and enamines; and
25 other heteroatoms in various other groups.

[0021] As used herein, the term “hydrocarbyl” refers to a functional group derived from a straight chain, branched, or cyclic hydrocarbon, such as an alkyl, alkenyl, alkynyl, aryl, cycloalkyl, acyl, or a combination thereof. A hydrocarbyl group can be unsubstituted or substituted.

30 [0022] The term “alkyl” as used herein refers to straight chain and branched alkyl groups and cycloalkyl groups having from 1 to about 20 carbon atoms, and typically from 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. Examples of straight chain alkyl groups include those with from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups
35 include, but are not limited to, isopropyl, isobutyl, sec-butyl, t-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. As used herein, the term “alkyl” encompasses all branched

chain forms of alkyl. Representative substituted alkyl groups can be substituted one or more times with any functional group, for example.

[0023] The term “alkenyl” as used herein refers to straight and branched chain and cyclic alkyl groups as defined herein, except that at least one double bond exists between two carbon atoms. Thus, alkenyl groups have from 2 to about 20 carbon atoms, and typically from 2 to 12 carbons or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to vinyl, $-\text{CH}=\text{CH}(\text{CH}_3)$, $-\text{CH}=\text{C}(\text{CH}_3)_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)$, $-\text{C}(\text{CH}_2\text{CH}_3)=\text{CH}_2$, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl, among others.

[0024] The term “resin” as used herein refers to polysiloxane material of any viscosity that includes at least one siloxane monomer that is bonded via a Si-O-Si bond to three or four other siloxane monomers. In one example, the polysiloxane material includes T or Q groups, as defined herein.

[0025] The term “number-average molecular weight” as used herein refers to the ordinary arithmetic mean of the molecular weight of individual molecules in a sample. It is defined as the total weight of all molecules in a sample divided by the total number of molecules in the sample. Experimentally, the number average molecular weight (M_n) is determined by analyzing a sample divided into molecular weight fractions of species i having n_i molecules of molecular weight M_i through the formula $M_n = \sum M_i n_i / \sum n_i$. The number average

molecular weight can be measured by a variety of well-known methods including gel permeation chromatography, spectroscopic end group analysis and osmometry.

[0026] The term “weight-average molecular weight” as used herein refers (M_w), which is equal to $\sum M_i^2 n_i / \sum M_i n_i$, where n_i is the number of molecules of molecular weight M_i . In various examples, the weight average molecular weight can be determined using light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

[0027] The term “radiation” as used herein refers to energetic particles travelling through a medium or space. Examples of radiation are visible light, infrared light, microwaves, radio waves, very low frequency waves, extremely low frequency waves, thermal radiation (heat), and black-body radiation.

[0028] The term “light” as used herein refers to electromagnetic radiation in and near wavelengths visible by the human eye, and includes ultra-violet (UV) light and infrared light, from about 10 nm to about 300,000 nm wavelength.

[0029] The term “cure” as used herein refers to exposing to radiation in any form, heating, or allowing to undergo a physical or chemical reaction that results in hardening, gelation, solidification or an increase in viscosity.

[0030] The term “pore” as used herein refers to a depression, slit, or hole of any size or shape in a solid object. A pore can run all the way through an object or partially through the object. A pore can intersect other pores.

[0031] The term “free-standing” or “unsupported” as used herein refers to a membrane with the majority of the surface area on each of the two major sides of the membrane not contacting a substrate, whether the substrate is porous or not. In some embodiments, a membrane that is “free-standing” or “unsupported” can be 100% not supported on both major sides. A membrane that is “free-standing” or “unsupported” can be supported at the edges or at the minority (e.g. less than about 50%) of the surface area on either or both major sides of the membrane.

[0032] The term “supported” as used herein refers to a membrane with the majority of the surface area on at least one of the two major sides contacting a substrate, whether the substrate is porous or not. In some embodiments, a membrane that is “supported” can be 100% supported on at least one side. A membrane that is “supported” can be supported at any suitable location at the majority (e.g. more than about 50%) of the surface area on either or both major sides of the membrane.

[0033] The term “enrich” as used herein refers to increasing in quantity or concentration, such as of a liquid, gas, or solute. For example, a mixture of gases A and B can be enriched in gas A if the concentration or quantity of gas A is increased, for example by selective permeation of gas A through a membrane to add gas A to the mixture, or for example by selective permeation of gas B through a membrane to take gas B away from the mixture.

[0034] The term “deplete” as used herein refers to decreasing in quantity or concentration, such as of a liquid, gas, or solute. For example, a mixture of gases A and B can be depleted in gas B if the concentration or quantity of gas B is decreased, for example by selective permeation of gas B through a membrane to take gas B away from the mixture, or for example by selective permeation of gas A through a membrane to add gas A to the mixture.

[0035] The term “solvent” as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0036] The term “selectivity” or “ideal selectivity” as used herein refers to the ratio of permeability of the faster permeating gas over the slower permeating gas, measured at room temperature.

[0037] The term “permeability” as used herein refers to the permeability coefficient (P_X) of substance X through a membrane, where $q_{mX} = P_X \cdot A \cdot \Delta p_X \cdot (1/\delta)$, where q_{mX} is the volumetric flow rate of substance X through the membrane, A is the surface area of one

major side of the membrane through which substance X flows, Δp_X is the difference of the partial pressure of substance X across the membrane, and δ is the thickness of the membrane. P_X can also be expressed as $V \cdot \delta / (A \cdot t \cdot \Delta p)$, wherein P_X is the permeability for a gas X in the membrane, V is the volume of gas X which permeates through the membrane, δ is the thickness of the membrane, A is the area of the membrane, t is time, Δp is the pressure difference of the gas X at the retente and permeate side. Permeability is measured at room temperature, unless otherwise indicated.

[0038] The term “permeance” as used herein refers to the normalized permeability (M_X) of substance X through a membrane, wherein $M_X = P_X / \delta = V / (A \cdot t \cdot \Delta p_X)$, wherein P_X is the permeability for a gas X in the membrane, V is the volume of gas X which permeates through the membrane, δ is the thickness of the membrane, A is the area of the membrane, t is time, Δp_X is the difference of the partial pressure of substance X across the membrane. Permeance is measured at room temperature, unless otherwise indicated.

[0039] The term “Barrer” or “Barrers” as used herein refers to a unit of permeability, wherein 1 Barrer = 10^{-11} (cm³ gas) cm cm⁻² s⁻¹ mmHg⁻¹, or 10^{-10} (cm³ gas) cm cm⁻² s⁻¹ cm Hg⁻¹, where “cm³ gas” represents the quantity of the gas that would take up one cubic centimeter at standard temperature and pressure.

[0040] The term “total surface area” as used herein with respect to membranes refers to the total surface area of the side of the membrane exposed to the feed gas mixture.

[0041] The term “air” as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

[0042] The term “room temperature” as used herein refers to a temperature of about 15 °C to 28 °C.

[0043] The term “coating” as used herein refers to a continuous or discontinuous layer of material on the coated surface, wherein the layer of material can penetrate the surface and can fill areas such as pores, wherein the layer of material can have any three-dimensional shape, including a flat or curved plane. In one example, a coating can be formed on one or more surfaces, any of which may be porous or nonporous, by immersion in a bath of coating material.

[0044] The term “surface” as used herein refers to a boundary or side of an object, wherein the boundary or side can have any perimeter shape and can have any three-dimensional shape, including flat, curved, or angular, wherein the boundary or side can be continuous or discontinuous. While the term surface generally refers to the outermost boundary of an

object with no implied depth, when the term 'pores' is used in reference to a surface, it refers to both the surface opening and the depth to which the pores extend beneath the surface into the substrate.

Hollow fiber.

5 **[0045]** In various embodiments, the present invention provides a method of forming a hollow fiber. The method can include providing or obtaining a substantially cylindrical solid core. The core can include a core composition. The core composition can include about 50 wt% to about 100 wt% of a composition that is at least one of meltable and sublimable. The method can include coating the core with a curable composition. The method can
10 include curing the curable composition. The method can include melting or subliming at least part of the core composition. The method can include removing at least part of the melted or sublimed part of the core composition. The method provides a hollow fiber. Various embodiments of the present invention provide a hollow fiber made by the method. In some embodiments, the method is a continuous method. In other embodiments, the
15 method is a batch-wise method.

[0046] Any suitable step can be included in the method of making a hollow fiber. In some examples, the core or supporting fiber is commercially acquired or otherwise acquired, whereas in other examples, the core or supporting is synthesized. In some embodiments, the melting or subliming at least part of the core composition can include using a solvent to
20 dissolve at least part of the core composition. The method can include any suitable number of steps before the hollow fiber is provided. For example, in embodiments including a supporting fiber, the method can include removing the supporting fiber from the hollow fiber after at least partial melting or sublimation of the core composition. The removing can be performed using any suitable method. In some examples, the removing
25 includes physically pulling the supporting fiber out from the hollow fiber, fully or partially dissolving the supporting fiber in a suitable solvent, melting or subliming the supporting fiber, or any combination thereof.

[0047] The hollow fiber can be any suitable hollow fiber. In some embodiments, the hollow fiber can include a cured polysiloxane composition, such as can be used for various
30 separation methods. The hollow fiber can have any suitable composition, length, diameter, or shape, as consistent with the method of making the fiber described herein. In some examples, the walls of the hollow fiber have a thickness, such as an average thickness or a thickness across the majority of the hollow fiber (e.g. equal to or greater than 50% of the length), of about 1 μm or less, or about 5 μm , 10 μm , 15 μm , 20 μm , 25 μm , 30 μm , 35 μm ,
35 40 μm , 45 μm , 50 μm , 55, 60, 65, 70, 80, 100, 150, or about 200 or more. In some examples, the walls of the hollow fiber have a thickness of about 1 μm to 200 μm , 5 μm to 120 μm , or about 10 μm range 60 μm .

[0048] In some embodiments, the method can be used to initiate a continuous procedure wherein the fiber is formed without a core.

Solid core.

[0049] In some embodiments, the method of making a hollow fiber can include providing or

5 obtaining a solid core. In some embodiments, the solid core can include at least one supporting fiber and a core composition coating the supporting fiber; in other embodiments, the solid core includes a core composition but no supporting fiber. The solid core is substantially solid, such that no liquid or no appreciable liquid is included in the solid core. The solidity of the core can be any suitable solidity, including substantially rigid, or a soft
10 solid such as a paste or a gel. The solid can be any suitable solid, such that the core is substantially nonflowable (e.g. viscosity greater than about 10,000 cP) under conditions of the coating and curing of the solid core. For example, the solid core can include a core composition that is a high viscosity liquid. In other embodiments, the solid core can include a core composition that is crystalline or an amorphous solid; e.g. a liquid that has a
15 temperature below the melting point of the core composition. The solid core can have any suitable shape, for example the solid core can be approximately or substantially cylindrical. As used herein, "substantially cylindrical" includes any cylindrical shape, including a cylindrical shape have a substantially smooth or untextured surface, or a cylindrical shape that has patterned or textured surface, wherein the pattern or texture is any suitable pattern or texture. Surface features of the cylinder can extend less than about 10% of the radius of
20 the cylinder away from the outer surface of the cylinder, or less than about 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, or less than about 1% of the radius of the cylinder away from the outer surface of the cylinder. In some embodiment, a pattern or texture can occur uniformly on the core; in other embodiments, a pattern or texture can be nonuniform, for
25 example can differ from location to location or can be interspersed with a smooth core. The substantially cylindrical core can be a round cylinder or a flattened cylinder. In some examples, the core has a diameter of about 10 μm or less, or about 100 μm , 150 μm , 200 μm , 250 μm , 300 μm , 350 μm , 400 μm , 450 μm , 500 μm , 550 μm , 600 μm , 1000 μm , 1500 μm , 2000 μm , 1 cm, or about 5 cm or more. In some embodiments the core has a
30 diameter of about 5 μm to 5 cm, 10 μm to 2000 μm , 50 μm to 800 μm , or about 100 μm to 400 μm .

[0050] In embodiments including a supporting fiber, the supporting fiber can be coated with the core composition such that the one or more fibers are located in any suitable position within the core composition. For example, the one or more supporting fibers can be
35 approximately in the middle of the composition coating the supporting fiber. In other examples, the one or more supporting fibers can be off-center or near an edge of the solid core. In some examples, the one or more supporting fibers can have a position within the

coated core that varies along the length of the coated core. In other embodiments, the one or more supporting fibers can have a substantially consistent position within the core composition along the length of the solid core. In some examples, the solid core includes one supporting fiber, or 2, 3, 4, 5, 6, 7, 8, 9, or 10 or more supporting fibers. In some
5 examples, the solid core includes one supporting fiber positioned in the center of the core composition substantially consistently along the length of the solid core. In some examples, the core composition can be coated on the supporting fiber substantially consistently along the majority of its length.

[0051] In some embodiments, the solid core is acquired commercially or otherwise; in

10 other embodiments, the method can include making the solid core. For example, in some embodiments providing or obtaining the core can include coating the supporting fiber with the core composition. The coating can occur in any suitable fashion. For example, the coating can occur by dipping or otherwise immersing the supporting fiber in the core composition. In some embodiments, the supporting fiber laden with core composition
15 material can be passed through a suitable die, draw plate, needle, or other suitable size-adjusting or shaping device to cause a consistent amount of material to be coated on the supporting fiber. In other embodiments, the supported fiber laden with core composition material can proceed directly to solidification without passing through any die or other size-adjusting or shaping device. In some embodiments, coating the supporting fiber with the
20 core composition can include at least one of immersion coating, die coating, extrusion, dipping, spraying, brushing, roll coating, and inkjet application.

[0052] In some embodiments providing or obtaining the core can include solidifying the core composition on the supporting fiber, or solidifying the core composition without the supporting fiber. The solidifying can occur in any suitable fashion. In some embodiments,
25 the solidifying occurs by sufficiently cooling the core composition-coated supporting fiber or the core composition without a supporting fiber such that the core composition solidifies. The solidification can be a transition from liquid or semi-liquid to a solid frozen state, e.g. the solidification can be a freezing of the core composition. In some embodiments, the solidification can be a transition of a thermoplastic material from a liquid or flowable state to
30 a solid or unflowable state. In some examples, the solidification can include a curing of the core composition, such as hydrosilylation curing, condensation curing, free-radical curing, amine-epoxy curing, radiation curing, cooling, or any combination thereof. The solidification can include any combination of freezing, thermoplastic transition to a solid unflowable state, or curing.

35 **[0053]** The cooling of the core composition can include cooling to any suitable temperature, such that the core composition becomes substantially solid or unflowable. The cooling can include cooling the core composition to a temperature at which the core

composition becomes a crystalline solid, an amorphous solid, or a high viscosity liquid that has low flowability or substantially no flowability under the conditions under which the curable material is coated on the solid core and subsequently cured. The cooling can include cooling to about -250 °C or less, or about 200 °C, 190 °C, 180 °C, 170 °C, 160 °C, 150 °C, 140 °C, 130 °C, 120 °C, 110 °C, 100 °C, 90 °C, 80 °C, 70 °C, 60 °C, 50 °C, 40 °C, 30 °C, 20 °C, 10 °C, 0 °C, or about 10 °C or higher. The cooling can include cooling to about -250 °C to 10 °C, -250 °C to -10 °C, or about -196 °C to -30 °C. The cooling can occur for any suitable amount of time, such as about 0.001 s to about 1 min, 0.01 to about 10 s, or about 0.1 s to about 5 s. In some embodiments, the cooling is performed by dipping the core composition-coated supporting fiber in a liquid gas, such as liquid nitrogen (e.g. about 196 °C) for a suitable amount of time.

[0054] After solidifying the core composition, the solid core can be subjected to any suitable treatment step or steps prior to being coated with the curable composition. In some embodiments, no further treatment steps occur. In other embodiments, the solid core can be sent through a die or another suitable size-adjusting or shaping apparatus, the solid core can be warmed, the solid core can be coiled and stored for a short or extended period, or any combination thereof.

Supporting fiber.

[0055] The solid core can include at least one supporting fiber and a core composition coating the supporting fiber. The supporting fiber can be any suitable supporting fiber and can have any suitable shape, diameter, and length, such that it can be used to form the solid core as described herein. In some examples, the supporting fiber can be provided on, for example, a spool or roll. In some examples, the supporting fiber may have a hollow core. In some examples, the supporting fiber has a diameter of about 5 μm or less, or about 10 μm, 20 μm, 50 μm, 75 μm, 100 μm, 125 μm, 150 μm, 175 μm, 200 μm, 225 μm, 250 μm, 275 μm, 300 μm, 325 μm, or about 350 μm or more. In some embodiments the supporting fiber has a diameter of about 5 μm to 1000 μm, 10 μm to 600 μm, or about 20 μm to 350 μm.

[0056] In some embodiments, the supporting fiber can have a melting or sublimation point that is higher than that of the core composition. In other embodiments, the supporting fiber can have a melting or sublimation point that is lower than that of the core composition. In some examples, the supporting fiber is substantially insoluble in at least one solvent that can dissolve the core composition. In some examples, the supporting fiber is substantially soluble in at least one solvent that can dissolve the core composition. In some embodiments, the supporting fiber is substantially soluble in at least one solvent that cannot dissolve or that can only minimally dissolve the cured curable composition coated on the solid core.

[0057] In some examples, the supporting fiber includes an organic polymer or copolymer. In some examples, the supporting fiber includes at least one of a polyoxymethylene, a polyoxymethylene copolymer with oxyethylene and others structural units, a polymethylmethacrylate (PMMA), a PMMA copolymer, a polystyrene, a polystyrene copolymer, a celluloid, a celluloid acetate, a cyclic olefin copolymer, an ethylene-vinyl acetate (EVA), an ethylene-vinyl alcohol (EVOH), a fluoroplastic, a PTFE, an acrylonitrile-butadiene-styrene (ABS), a polyacrylate, a polyamide, a polyamide-imide, a polyimide, a poetherimide, a polysulfone, a polyethersulfone, a polyketone, a polyaramide, a polyetheretherketone (PEEK), a polycarbonate, a polyester, a polycaprolactone, a polybutylene terephthalate, a polyurethane, a polyurea, a polyurethane-urea copolymer, a polyethylene terephthalate, a polylactic acid, a polyphenylene oxide, a polyphenylene sulfide, a thermoplastic polyurethane, a Kevlar™, a polyvinylacetate (PVA), a polyvinyl chloride (PVC), a polyvinylidene chloride (PVDC), and a styrene-acrylonitrile (SAN) copolymer. In some embodiments, the supporting fiber includes at least one of polypropylene, poly(vinyl alcohol), and monofilament water-wettable fiber such as Nylon 6,6, Nylon 6,12 or polyethylene terephthalate.

Core composition.

[0058] The solid core can include a core composition. In some embodiments, the core composition coats the at least one supporting fiber; in other embodiments, the core composition has no supporting fiber. The core composition can be any suitable core composition such that it can be solidified suitably for coating of the solid core with the curable composition, subsequent curing, and such that it can be at least partially melted or sublimed after the curing. In various embodiments, the core composition can be formed without a supporting fiber or coated on a supported fiber with any suitable thickness and shape, such that the solidified core or the supporting fiber and solidified core form a solid core having a suitable diameter. In some embodiments, the solid core includes a frozen liquid. In some embodiments, the solid core includes a sublimable solid below its sublimation temperature. In some embodiments, the solid core includes a volatile solvent that is gelled by a minority fraction of a gel-inducing polymer or polymer network, such as a hydrogel or gelled organic solvent or gelled organosiloxane liquid.

[0059] The core composition can include any suitable proportion of sublimable or meltable material; the entire core composition need not be sublimable or meltable. In some embodiments, the core composition is substantially all meltable or sublimable. In other embodiments, about 50 wt% or less of the core composition is a meltable or sublimable composition, or about 55 wt%, 60 wt%, 65 wt%, 70 wt%, 75 wt%, 80 wt%, 85 wt%, 90 wt%, 91 wt%, 92 wt%, 93 wt%, 94 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, or about 100 wt% of the core composition is a meltable or sublimable composition (e.g. at least one of

meltable or sublimable). In some examples, about 50-100 wt% of the core composition is meltable or sublimable, or about 90-100 wt%, or about 95-100 wt%. In some embodiments, a component can be described as meltable at a particular temperature if the component has a zero shear viscosity of about 10,000 cP or less, or about 1000 cP, 500 cP, 400 cP, 300 cP, 200 cP, 100 cP, 90 cP, 80 cP, 70 cP, 60 cP, 50 cP, 40 cP, 30 cP, 20 cP, or about 10 cP or less at that temperature, or a zero shear viscosity of about 1-10,000 cP, 1-1,000 cP, 1-100 cP, 1-50 cP, or about 1-10 cP at that temperature.

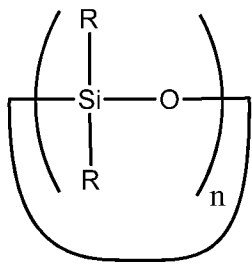
[0060] In some embodiments, the meltable or sublimable composition can have a melting or sublimation point that is higher than that of the supporting fiber. In other embodiments, the meltable or sublimable composition can have a melting or sublimation point that is lower than that of the supporting fiber. In some examples, the core composition is substantially insoluble in at least one solvent that can dissolve the supporting fiber. In some examples, the core composition is substantially soluble in at least one solvent that can dissolve the supporting fiber. In some embodiments, the core composition is substantially soluble in at least one solvent that cannot dissolve or that can only minimally dissolve the cured curable composition coated on the solid core.

[0061] In various embodiments, the meltable or sublimable composition is meltable or sublimable at about -200 °C or less, or about -190 °C, -180 °C, -170 °C, -160 °C, -150 °C, -140 °C, -130 °C, -120 °C, -110 °C, -100 °C, -90 °C, -80 °C, -70 °C, -60 °C, -50 °C, -40 °C, -30 °C, -20 °C, -10 °C, 0 °C, 10 °C, 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, or about 200 °C or higher. In some examples, the meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 °C to about 200 °C, or about -150 °C to about 150 °C, or about 0 °C to 60 °C, 0 °C to 35 °C, or at about -200 °C to about 50 °C, 40 °C, 30 °C, 20 °C, 10 °C, 0 °C, 5 °C, 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, or to about 80 °C or more. In some examples, at at least one temperature from about -200 °C to -200 °C, -150 °C to 150 °C, 0 to 60 °C, or about 0 °C to 35 °C, the meltable or sublimable composition has a zero shear viscosity of about 10,000 cP or less, or about 1000 cP, 500 cP, 400 cP, 300 cP, 200 cP, 100 cP, 90 cP, 80 cP, 70 cP, 60 cP, 50 cP, 40 cP, 30 cP, 20 cP, or about 10 cP or less. In some examples, at about 25 °C, the meltable or sublimable composition has a zero shear viscosity of about 500 cP or less, 400 cP, 300 cP, 200 cP, 100 cP, 90 cP, 80 cP, 70 cP, 60 cP, 50 cP, 40 cP, 30 cP, 20 cP, or about 10 cP or less. In some embodiments, between about 0 °C and about 35 °C, about 100 wt% of the meltable or sublimable composition, or about 95 wt%, 90 wt%, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or about 5 wt% of the meltable or sublimable composition has a viscosity of about 0-10,000 cP, 0-1,000 cP, 0-100 cP, 0-50 cP, or about 0-10 cP.

[0062] In various examples, the core composition can include at least one of water, an organocyclosiloxane, a hydrogel polymer, and a curable silicone composition. The curable silicone composition can be any suitable curable composition described herein, such as an organosilicon curable composition, such a hydrosilylation curable silicone composition, provided that the solidified core composition is at least partially meltable or sublimable. In some embodiments, the core composition includes less than about 30 wt% of the hydrogel polymer, or less than about 25 wt%, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or less than about 0.1 wt% of the hydrogel polymer; in some examples, the remainder or majority of the remainder of the core composition can be water, such as about 75-99.9 wt% water, about 85-99 wt% water, or about 93-98 wt% water. In some examples, the core composition includes about 0-30 wt% of the hydrogel polymer, 1-20 wt%, or about 2-10 wt% of the hydrogel polymer. In some embodiments, the core composition includes less than about 30 wt% of a curable silicone composition, or less than about 25 wt%, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 wt%, or less than about 0.1 wt% of the curable silicone composition such as a hydrosilylation curable composition; in some examples, the remainder of the majority of the remainder of the core composition can be a organocyclopolsiloxane, such as octamethylcyclotetrasiloxane, such as about 75-99.9 wt% organocyclopolsiloxane, about 85-99 wt% organocyclopolsiloxane, or about 93-98 wt% organocyclopolsiloxane.

[0063] In various embodiments, the hydrogel polymer can include any suitable polymer than can form a hydrogel, such as a poly(ethylene glycol), a poly(vinylpyrrolidone), a polyacrylamide, a poly(hydroxyethylmethacrylate), a polyvinyl alcohol, a polyglycol, a polyethylene glycol dimethacrylate, a polyethylene glycol diacrylate, a polyhydroxyethyl methacrylate, a polyacrylic acid, a hydrolyzed polyacrylonitrile, a polyethyleneimine, an ethoxylated polyethyleneimine, a polyallyl alcohol, a polyallylamine, copolymers thereof, a poly(ethylene-co-vinyl alcohol), a gelatin, or combinations thereof.

[0064] The organocyclosiloxane can be any suitable organocyclosiloxane. In various embodiments, the organocyclosiloxane can include about 3 to 6, 3 to 10, or about 3 to 12 di(C₁₋₅alkyl)siloxane repeating units. In some examples the organocyclosiloxane can have the formula



wherein n is about 3 to about 12 (e.g., the organocyclosiloxane contains [R₂SiO₂/2] units),

wherein each R at each occurrence is independently selected from C₁₋₅alkyl. In some examples, the organocyclosiloxane can have 3 to 12 dimethylsiloxane repeating units. In some embodiments, the organocyclosiloxane can be hexa(C₁₋₅alkyl)cyclotrisiloxane, octa(C₁₋₅alkyl)cyclotetrasiloxane, deca(C₁₋₅alkyl)cyclopentasiloxane, dodeca(C₁₋₅alkyl)cyclohexasiloxane, or any combination thereof, wherein each C₁₋₅alkyl group at each occurrence is independently selected or the same and can be substituted or unsubstituted; for example, each C₁₋₅alkyl group at each occurrence is individually chosen from methyl, ethyl, propyl, butyl, and pentyl. In various examples, the organocyclosiloxane can be hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6), or any combination thereof.

Coating the core.

[0065] The method of making a hollow fiber can include coating the core with a curable composition. The coated core can have any suitable shape, for example the coated core can be approximately or substantially cylindrical. In some examples, the coated core has a diameter of about 10 μm or less, or about 100 μm, 150 μm, 200 μm, 250 μm, 300 μm, 350 μm, 400 μm, 450 μm, 500 μm, 550 μm, 600 μm, 1000 μm, 1500 μm, 2000 μm, 1 cm, or about 5 cm or more. In some embodiments the coated core has a diameter of about 5 μm to 5 cm, 10 to 2000 μm, 50 to 800 μm, or about 100 to 400 μm.

[0066] The coating can be a continuous coating along the length and circumference of the solid core. The coating can have a substantially even thickness around the circumference of the solid core and along the length of the solid core. The curable composition can be coated on the solid core substantially consistently along the majority of its length. For example, the solid core can be approximately in the middle of the curable composition coating the solid core. The solid core can have a substantially consistent position within the curable composition coating. In other examples, the solid core can be off-center or near an edge of the curable composition coating. The solid core can have a position within the curable composition that varies along the length of the coated core.

[0067] The coating can occur in any suitable fashion. For example, the coating can occur by dipping or otherwise immersing the solid core in the curable composition. In some embodiments, the solid core laden with curable composition material can be passed through a suitable die, draw plate, needle, or other suitable size-adjusting or shaping device to cause a consistent amount of material to be coated on the solid core. In other embodiments, the solid core laden with the curable composition can proceed directly to curing or another step without passing through any die or other size-adjusting or shaping device. In some embodiments, coating the solid core with the curable composition can

include at least one of immersion coating, die coating, extrusion, dipping, spraying, brushing, roll coating, and inkjet spraying.

Curable composition.

[0068] The method of making a hollow fiber can include coating the solid core with a curable composition. The curable composition can be any suitable curable composition, such that the curable composition can be used to generate a hollow fiber using the method described herein. In some examples, the core composition can include a suitable curable composition, such as a suitable hydrosilylation curable composition, such that solid core can be used to generate hollow fibers as described herein. In various examples, the curable composition includes at least one of a hydrosilylation-curable composition, a condensation curable composition, a free-radical curable composition, an amine-epoxy curable composition, a radiation curable composition, a cooling-curable composition, a vapor-curable composition or any combination thereof. In some embodiments, the curing can occur at room temperature or at any suitable temperature below room temperature, such as at a temperature wherein the meltable or sublimable core composition is substantially unmelted and unsublimed.

[0069] In some embodiments, the curable composition is a curable organosilicon composition. The curing of the curable organosilicon composition gives a cured product of the organosilicon composition. The curable organosilicon composition includes suitable ingredients to allow the composition to be curable in a suitable fashion. In addition to the at least one suitable polysiloxane, the organosilicon composition can include any suitable additional ingredients, including any suitable organic or inorganic component, including components that do not include silicon, including components that do not include a polysiloxane structure. In some examples, the cured product of the organosilicon composition includes a polysiloxane.

[0070] The curable organosilicon composition includes molecular components that have properties that allow the composition to be cured. In some embodiments, the properties that allow the curable organosilicon composition to be cured are specific functional groups. In some embodiments, an individual compound contains functional groups or has properties that allow the curable organosilicon composition to be cured by one or more curing methods. In some embodiments, one compound can contain functional groups or have properties that allow the curable organosilicon composition to be cured in one fashion, while another compound can contain functional groups or have properties that allow the curable organosilicon composition to be cured in the same or a different fashion. The functional groups that allow for curing can be located at pendant or, if applicable, terminal positions in the compound.

[0071] The curable organosilicon composition includes any suitable organosilicon

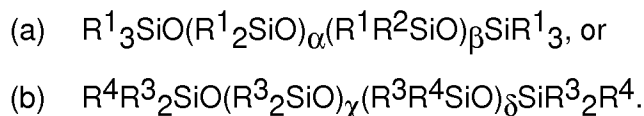
compound. The organosilicon compound can be, for example, a silane, polysilane, siloxane, or a polysiloxane, such as any suitable one of such compound as known in the art. The curable organosilicon composition can contain any number of suitable organosilicon compounds, and any number of other suitable organic compounds. An organosilicon compound can include any functional group that allows for curing.

[0072] In some embodiments, the organosilicon compound can include a silicon-bonded hydrogen atom, such as organohydrogensilane or an organohydrogensiloxane. In some embodiments, the organosilicon compound can include an alkenyl group, such as an organoalkenylsilane or an organoalkenyl siloxane. In other embodiments, the organosilicon compound can include any functional group that allows for curing. The organosilane can be a monosilane, disilane, trisilane, or polysilane. Similarly, the organosiloxane can be a disiloxane, trisiloxane, or polysiloxane. The structure of the organosilicon compound can be linear, branched, cyclic, or resinous. Cyclosilanes and cyclosiloxanes can have from 3 to 12 silicon atoms, alternatively from 3 to 10 silicon atoms, alternatively from 3 to 4 silicon atoms.

[0073] In one example, an organohydrogensilane can have the formula $HR^1_2Si-R^2-SiR^1_2H$, wherein R^1 is C_{1-10} hydrocarbyl or C_{1-10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, linear or branched, and R^2 is a hydrocarbylene group free of aliphatic unsaturation having a formula selected from monoaryl such as 1,4-disubstituted phenyl, 1,3-disubstituted phenyl; or bisaryl such as 4,4'-disubstituted-1,1'-biphenyl, 3,3'-disubstituted-1,1'-biphenyl, or similar bisaryl with a hydrocarbon chain including 1 to 6 methylene groups bridging one aryl group to another.

[0074] The organosilicon compound can be an organopolysiloxane compound. In some examples, the organopolysiloxane compound has an average of at least one, two, or more than two functional groups that allow for curing. The organopolysiloxane compound can have a linear, branched, cyclic, or resinous structure. The organopolysiloxane compound can be a homopolymer or a copolymer. The organopolysiloxane compound can be a disiloxane, trisiloxane, or polysiloxane.

[0075] In one example, an organopolysiloxane can include a compound of the formula



[0076] In formula (a), α has an average value of about 0 to about 2000, and β has an average value of about 2 to about 2000. Each R^1 is independently a monovalent functional group. Suitable monovalent functional groups include, but are not limited to, acrylic groups; alkyl; halogenated hydrocarbon groups; alkenyl; alkynyl; aryl; and cyanoalkyl. Each R^2 is independently a functional group that allows for curing of the

silicone composition, or R¹.

[0077] In formula (b), χ has an average value of 0 to 2000, and δ has an average value of 0 to 2000. Each R³ is independently a monovalent functional group. Suitable monovalent functional groups include, but are not limited to, acrylic groups; alkyl; halogenated

5 hydrocarbon groups; alkenyl; alkynyl; aryl; and cyanoalkyl. Each R⁴ is independently a functional group that allows for curing of the silicone composition, or R³.

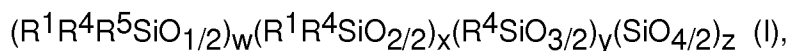
[0078] An organopolysiloxane compound can contain an average of about 0.1 mole% to about 100 mole% of functional groups that allow for curing of the silicone composition, and any range of mole% therebetween. The mole percent of functional groups that allow for

10 curing of the silicon composition in the resin is the ratio of the number of moles of siloxane units in the resin having a functional group that allows for curing of the silicone composition to the total number of moles of siloxane units in the organopolysiloxane, multiplied by 100.

[0079] The curable organosilicon composition can include a single organopolysiloxane or a combination including two or more organopolysiloxanes that differ in at least one of the

15 following properties: structure, viscosity, average molecular weight, siloxane units, and sequence.

[0080] Examples of organopolysiloxanes can include compounds having the average unit formula



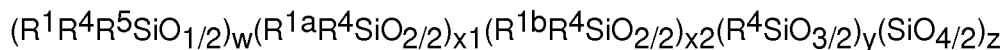
20 wherein R¹ is a functional group independently selected from any optionally further substituted C₁₋₁₅ functional group, including C₁₋₁₅ monovalent aliphatic hydrocarbon groups, C₄₋₁₅ monovalent aromatic hydrocarbon groups, and monovalent epoxy-

substituted functional groups, R⁴ is a functional group that allows for curing of the silicone composition or R⁵ or R¹, R⁵ is R¹ or R⁴, 0 ≤ w < 0.95, 0 ≤ x < 1, 0 ≤ y < 1, 0 ≤ z < 0.95, and

25 w + x + y + z ≈ 1. In some embodiments, R¹ is C₁₋₁₀ hydrocarbyl or C₁₋₁₀ halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, or C₄ to C₁₄ aryl. In some embodiments, w is from 0.01 to 0.6, x is from 0 to 0.5, y is from 0 to 0.95, z is from 0 to 0.4, and w + x + y + z ≈ 1.

[0081] In descriptions of average unit formula, such as formula I, the subscripts w, x, y, and z are mole fractions. It is appreciated that those of skill in the art understand that for the average unit formula (I), the variables R¹, R⁴, and R⁵ can independently vary between individual siloxane formula units. Alternatively, the variables R¹, R⁴, and R⁵ can independently be the same between individual siloxane formula units. For example, average unit formula (I) above can include the following average unit formula:

30



wherein subscripts $x1+x2 = x$, and where R^{1a} is not equal to R^{1b} . Alternatively, R^{1a} can be equal to R^{1b} .

[0082] In some embodiments, the curable composition includes a free radical initiator, such as a peroxide, azo-nitrile, or organoborane-based compound. In some embodiments, the curable composition includes a photoacid generator or photosensitizer. In some embodiments, the curable composition includes an organoborane-organonitrogen. In some embodiments, the curable composition is a hot-melt composition that cures upon cooling.

Optional ingredients.

[0083] Any optional ingredient described herein can be present in the hollow fiber, in the curable composition that is coated on the core, on in the core composition; alternatively, any optional ingredient described herein can be absent from the hollow fiber, the curable composition that is coated on the core, on from the core composition. Without limitation, examples of such optional additional components include surfactants, emulsifiers, dispersants, polymeric stabilizers, crosslinking agents, combinations of polymers, crosslinking agents, catalysts useful for providing a secondary polymerization or crosslinking of particles, rheology modifiers, density modifiers, aziridine stabilizers, cure modifiers such as hydroquinone and hindered amines, free-radical initiators, anti-foaming agents, polymers, diluents, acid acceptors, antioxidants, heat stabilizers, flame retardants, scavenging agents, silylating agents, foam stabilizers, solvents, diluents, plasticizers, fillers and inorganic particles, pigments, dyes and dessicants. Liquids can optionally be used. An example of a liquid includes water, an organic solvent, any liquid organic compound, a silicone liquid, organic oils, ionic fluids, and supercritical fluids. Other optional ingredients include polyethers having at least one alkenyl group per molecule, thickening agents, fillers and inorganic particles, stabilizing agents, waxes or wax-like materials, silicones, organofunctional siloxanes, alkylmethylsiloxanes, siloxane resins, silicone gums, silicone carbinol fluids can be optional components, water soluble or water dispersible silicone polyether compositions, silicone rubber, hydrosilylation catalyst inhibitors, adhesion promoters, heat stabilizers, UV stabilizers, and flow control additives.

Curing the curable composition.

[0084] The method of making a hollow fiber can include curing the curable composition coated on the core. The curing can be any suitable curing. For example, the curing can include hydrosilylation curing, condensation curing, free-radical curing, amine-epoxy curing, radiation curing, cooling, or any combination thereof. In various embodiments, curing includes exposing the curable composition-coated solid core to radiation such as heat or light. In some embodiments, the curing includes heating the curable composition to

about -196 °C or less, 150 °C, 125 °C, 100 °C, 75 °C, 50 °C, 25 °C, 0 °C, 25 °C, 50 °C, 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, or about 200 °C or more. In some embodiments, the curing includes heating the curable composition to about -200 °C to about 200 °C, -40 °C to about 35 °C, or about 0 °C to about 25 °C. Heating can be performed in any suitable fashion. In some embodiments, the coated core is passed through a heated area for a sufficient duration of time that the curing of the curable composition occurs. In some examples, the coated core is heated for about 0.01 s or less, 1 s, 5 s, 30 s, 1 min, 5 min, 30 min, or about 1 hour or more. In some embodiments, the curable-composition coated solid core is heated for about 0.0001 s to about 1 h, 0.001 to 1 min, or about 0.01 s to about 5 s. The heating can be performed using any conventional method, such as by passing the material an oven, a heated pipe, or by otherwise exposing to any suitable form of radiation.

[0085] Various methods of curing can be used, including any suitable method of curing, including for example hydrosilylation curing, condensation curing, free-radical curing, amine-epoxy curing, radiation curing, cooling, or any combination thereof. A composition that is cured via one curing method can be cured by other curing methods in addition to the one curing method. The curable composition, such as a curable organosilicon composition, can include molecules with properties that allow one curing method, as well as molecules that allow different curing methods. In some embodiments, the curable organosilicon composition can include multiple features on the same molecule that allow the composition to be cured via one curing method and cured via other curing methods, and in some embodiments, the organosilicon composition can include features that allow it to be cured via one curing method on one molecule and features that allow it to be curing via other curing methods on a different molecule.

[0086] A curable composition that is curable via a particular method can include other compounds curable via the particular method in addition to organosilicon compounds. In some embodiments, the other compounds curable via the particular curing method can participate with the organosilicon compounds curable via the particular curing method during the application of the particular curing method. In other embodiments, the other compounds curable via the particular curing method do not participate with the organosilicon compounds curable via the particular curing method during performance of the particular curing method.

[0087] In hydrosilylation curing, for example, an organosilicon compound that includes a silicon atom with a silicon-bonded hydrogen atom reacts with an unsaturated group such as an alkenyl group, adding across the unsaturated group and causing the unsaturated group to lose at least one degree of unsaturation (e.g. a double bond is converted to a single bond), such that the silicon atom is bound to one carbon atom of the originally

unsaturated group, and the hydrogen atom is bound to the other carbon atom of the originally unsaturated group. Having an average of at least two unsaturated groups on one or more molecules and an average of greater than two silicon-bonded hydrogen atoms on one or more molecules can help cross-linking to occur. In another example, having an average of greater than two unsaturated groups on one or more molecules and an average of at least two silicon-bonded hydrogen atoms on one or more molecules can help cross-linking to occur. In one example, a curable organosilicon composition that is hydrosilylation curable can include a compound having an average of at least two unsaturated groups per molecule; an organosilicon compound having an average of at least two silicon-bonded hydrogen atoms per molecule; and an optional hydrosilylation catalyst. In some embodiments, the hydrosilylation catalyst is present. In other embodiments, the hydrosilylation catalyst is not present. In some embodiments, the unsaturated groups are alkenyl groups.

[0088] In some embodiments, the hydrosilylation catalyst can be any hydrosilylation catalyst including a platinum group metal or a compound containing a platinum group metal. Platinum group metals can include platinum, rhodium, ruthenium, palladium, osmium and iridium. Examples of hydrosilylation catalysts include the complexes of chloroplatinic acid and certain vinyl-containing organosiloxanes disclosed by Willing in U.S. Pat. No. 3,419,593, such as the reaction product of chloroplatinic acid and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; microencapsulated hydrosilylation catalysts including a platinum group metal encapsulated in a thermoplastic resin, as exemplified in U.S. Pat. No. 4,766,176 and U.S. Pat. No. 5,017,654; and photoactivated hydrosilylation catalysts, such as platinum(II) bis(2,4-pentanedioate), as exemplified in U.S. Patent No. 7,799,842. An example of a suitable hydrosilylation catalyst can include a platinum(IV) complex of 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane. One example of a suitable hydrosilylation catalyst is Karstedt's catalyst.

[0089] In another embodiment, the hydrosilylation catalyst can be at least one photoactivated hydrosilylation catalyst. The photoactivated hydrosilylation catalyst can be any of the well-known hydrosilylation catalysts including a platinum group metal or a compound containing a platinum group metal. The suitability of particular photoactivated hydrosilylation catalyst for use in an organosilicon composition of the present invention can be readily determined by routine experimentation.

[0090] The concentration of the hydrosilylation catalyst can be sufficient to catalyze hydrosilylation of the curable organosilicon composition, for example sufficient to catalyze the addition reaction (hydrosilylation) of an organosilicon compound having an average of at least two silicon-bonded hydrogen atoms per molecule with an organopolysiloxane having an average of at least two silicon-bonded alkenyl groups per molecule. Typically,

the concentration of the hydrosilylation catalyst is sufficient to provide from about 0.1 to about 1000 ppm of a platinum group metal, from about 0.5 to about 500 ppm of a platinum group metal, and more preferably from about 1 to about 100 ppm of a platinum group metal, based on the total weight of the uncured composition. The rate of cure can be very slow below about 0.1 ppm of platinum group metal. The use of more than 1000 ppm of platinum group metal is possible, but is generally undesirable because of catalyst cost.

[0091] In condensation curing, for example, an organosilicon compound that includes a silicon-bonded hydrolysable group reacts with water to form a hydroxy-substituted silicon atom. The reactive hydroxy group can then attack other silicon atoms, including other silicon atoms with hydrolysable groups or with hydroxy groups, forming a polysiloxane. In some embodiments, the silicon atom that is attacked by the reactive hydroxy group can have a protonated hydroxy group or a hydrolysable group, wherein the protonated hydroxy group or the hydrolysable group is a good leaving group. In some embodiments, water is not required to hydrolyze a hydrolysable group, but rather a reactive hydroxy-substituted organosilicon is already present in the curable organosilicon composition, which can attack other silicon atoms, including silicon atoms with hydroxy groups or silicon atoms with hydrolysable groups. An acid or base catalyst is an optional component in condensation curable organosilicon compositions, such as any suitable organic or mineral acid, or any suitable base. In some embodiments, an acid or base catalyst is present. In other embodiments, an acid or base catalyst is not present.

[0092] A condensation curable organosilicon composition can include an organosilicon with at least one silicon-substituted hydrolysable group, or with at least one silicon-substituted hydroxy group. The organosilicon can be a silane, a polysilane, a siloxane, or a polysiloxane. The organosilicon can include an average of one silicon-substituted hydrolysable group per molecule, an average of two silicon-substituted hydrolysable groups per molecule, or more.

[0093] A hydrolysable group can be a group that reacts with water in the absence of a catalyst at any temperature from room temperature to 100 °C within several minutes, for example thirty minutes, to form a silanol (Si-OH) group, or another hydroxy-substituted group. Examples of hydrolysable groups can include, but are not limited to, -Cl, -Br, -OR⁷, -OCH₂CH₂OR⁷, CH₃C(=O)O-, Et(Me)C=N-O-, CH₃C(=O)N(CH₃)-, and -ONH₂, wherein R⁷ is C₁ to C₈ hydrocarbyl or C₁ to C₈ halogen-substituted hydrocarbyl. In one example, a condensation curable organosilicon composition includes one or more of the following: Me₂ViSiCl, Me₃SiCl, MeSi(OEt)₃, PhSiCl₃, MeSiCl₃, Me₂SiCl₂, PhMeSiCl₂, SiCl₄, Ph₂SiCl₂, PhSi(OMe)₃, MeSi(OMe)₃, PhMeSi(OMe)₂, and Si(OEt)₄, wherein Me is methyl, Et is ethyl, and Ph is phenyl.

[0094] Optionally, a condensation curable composition can include a condensation catalyst. In some embodiments, a condensation catalyst is present. In other embodiments, a condensation catalyst is not present. Examples of condensation catalysts include, for example, amines, and complexes of lead, tin, zinc, titanium, zirconium, aluminum and iron with carboxylic acids. In one example, 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.

[0095] In free-radical curing, for example, a free-radical is generated. The free-radical then can attack a free-radical polymerizable functional group. The attacking group forms a bond to the free-radical polymerizable group, and transfers a radical thereto. The free-radical polymerizable functional group can then go on to attack other free-radical polymerizable functional groups.

[0096] A free-radical curable organosilicon composition can include an organosilicon with at least one free-radical polymerizable group. The organosilicon can be a silane, a polysilane, a siloxane, or a polysiloxane. The organosilicon can include an average of one free-radical polymerizable group per molecule, an average of two free-radical polymerizable groups per molecule, or more. In some embodiments, a free-radical curable organosilicon composition can include an organic compound that does not include silicon that has at least one free-radical polymerizable group. The organic compound that does not include silicon can include an average of one free-radical polymerizable groups per molecule, an average of two free-radical polymerizable groups per molecule, or more. Examples of free-radical polymerizable groups include, for example, alkenyl groups and alkynyl groups, as well as groups such as ethers, ketones, aldehydes, carboxylates, ketals, acetals, cyano groups, nitro groups, or halogens.

[0097] Free-radicals can be generated by any suitable method. Free radicals can be initiated by, for example, thermal decomposition, photolysis, redox reactions, persulfates, ionizing radiation, electrolysis, plasma, sonication, chemical decomplexation, or a combination thereof. In one example, a free-radical is generated using a free-radical initiator. A free-radical initiator is an optional ingredient. In some embodiments, a free-radical initiator is present. In other embodiments, a free-radical initiator is not present. In one example, the free-radical initiator can be a free-radical photoinitiator, an organic peroxide, or a free-radical initiator activated by heat. Further, a free-radical photoinitiator can be any free radical photoinitiator capable of initiating cure (cross-linking) of the free-radical polymerizable functional groups upon exposure to radiation, for example, having a wavelength of from 200 to 800 nm. In another example, the free-radical initiator is a organoborane free-radical initiator. In one example, the free-radical initiator can be an organic peroxide. For example, elevated temperatures can allow a peroxide to decompose

and form a highly reactive radical, which can initiate free-radical polymerization. In some examples, decomposed peroxides and their derivatives can be byproducts. In some embodiments, the curable composition comprises an organoborane-organonitrogen complex capable of forming free radicals that is activated without heat or radiation by mixing or exposing to decomplexing compound to initiate the free radical curing condition. In some embodiments, the curable compound is cured by exposing the composition to a volatile decomplexing compound such as acetic acid (as a liquid or vapor). The free-radical photoinitiator can be a single free-radical photoinitiator or a mixture comprising two or more different free-radical photoinitiators. The concentration of the free-radical photoinitiator can be from 0.1 to 6% (w/w), alternatively from 1 to 3% (w/w), based on the weight of the silicon compounds in the free-radical curable organosilicon composition. One example of a free-radical initiator, which can operate thermally or with light activation, is VAROX DCBP-50 which includes bis(2,4-dichlorobenzoyl) peroxide, 50% in silicone oil.

[0098] In amine-epoxy curing, for example, a primary- or secondary-amine reacts with an epoxy compound to produce, for example, aminoalcohols. The epoxy-containing compound can be an organosilicon compound, or an organic compound that does not include silicon. The primary- or secondary-amine-containing compound can be an organosilicon, or an organic compound that does not include silicon. An amine-functional compound can be an amine-functionalized organopolysiloxane.

[0099] In an example, an amine-epoxy curable composition includes an epoxy-functional organosilicon compound and an amino-functional curing agent. In one example, the epoxy-functional organosilicon compound is a polysiloxane compound. The epoxy-functional organosilicon compound can have an average or at least two silicon-bonded epoxy-substituted functional groups per molecule and the curing agent can have an average of at least two nitrogen-bonded hydrogen atoms per molecule.

[00100] Radiation that can be used for radiation curing includes, for example, visible light, infrared light, microwaves, radio waves, very low frequency waves, extremely low frequency waves, thermal radiation (heat), and black-body radiation. Any of the curing methods disclosed herein can include radiation curing; for example, any of the curing methods disclosed herein can include the application of heat or light. For example, any of a hydrosilylation curable composition, a condensation curable composition, an epoxy-amine curable composition, or a composition curable by cooling, a free-radical curable composition, can include one or more steps that include the application of radiation, and the application of radiation to the curable composition can initiate, assist, or cause the chemical or physical processes that are part of the curing process. In some embodiments, any of hydrosilylation curing, condensation curing, epoxy-amine curing, free-radical curing, or curing via cooling can also be described as radiation curing, due to the application of

radiation during the curing process. In other embodiments, any of hydrosilylation curing, condensation curing, epoxy-amine curing, free-radical curing, or curing via cooling are not described as radiation curing, due to the lack of applied radiation during the curing process.

[00101] In some embodiments, the curable composition is a hot-melt composition that cures upon cooling. In one example of cooling giving a cured product of an organosilicon composition, an organosilicon composition that essentially has a liquid flowable state is cooled at least as low as room temperature to give an organosilicon composition that essentially has a solid nonflowable state. Organosilicon compositions that include compounds that can behave as thermoplastics are an example of silicon composition that can be cooled to give a cured product of the silicon composition. The compound that behaves as a thermoplastic can be a polymer.

Melting or subliming the core composition.

[00102] The method of making a hollow fiber can include melting or subliming the core composition. The melting or subliming can be any suitable melting or subliming, provided that the melting or subliming provides a hollow fiber membrane or is at least one step in providing a hollow fiber membrane.

[00103] The melting or subliming can be partial melting or subliming, such that less than 100% of the core composition melts or sublimes. In some embodiments, the melting or subliming can be substantially complete melting or sublimation of the core composition. In some embodiments, less than 100% of the core composition is meltable or sublimable; in some examples the melting or subliming can leave behind nonmeltable or nonsublimable components of the core composition while removing some or substantially all of the meltable or sublimable components. In some examples, nonmeltable or nonsublimable components of the core composition, or meltable or sublimable components of the core composition that were not melted or sublimed, can remain behind in the hollow fiber without being removed; in other examples, the remaining material can be partially or substantially fully removed using other techniques. In some examples, removing the support fiber from the hollow fiber can at least partially remove remaining material from the hollow fiber.

[00104] The melting or subliming can include heating the coated core or allowing the coated core to warm to a higher temperature. In some examples, the melting or subliming can include placing the coated core in a vacuum. In various embodiments, the melting or subliming can include placing the coated core in a heated environment such as an oven and allowing the coated core to rise to a temperature at which melting or sublimation occurs, such as about -50 °C or less, or about 10 °C, 25 °C, 35 °C or about 60 °C or more.

[00105] Removal of the at least part of the melted or sublimed part of the core composition can be performed in any suitable way. For example, the melted core composition can

emerge from an end of the hollow fiber; in some examples, air pressure, solvent washing, rolling the hollow fiber between rollers, or any other suitable method can be used to induce the melted core composition to emerge from the end of the hollow fiber. In some examples, the melted core composition can move through the hollow fiber to the exterior of the hollow fiber, where it can be wiped or washed away. In some examples, a liquid can be contacted to the outside of the hollow fiber that helps to draw out the melted core composition. In some examples, a liquid that can permeate the membrane such as a suitable solvent can be applied, which can help to dilute the melted core composition and push it out the ends of the fiber or which can dissolve unmelted or partially melted core composition for flushing out the ends of the fiber or diffusion through the fiber.

[00106] In some embodiments, a solvent can be used before, during, or after the melting or subliming to dissolve at least part of the core composition or the support fiber. In some embodiments, a solvent can be used to remove at least part of the core composition after it has at least partially melted or sublimed; in some embodiments, the solvent can be used to help flush out melted core material from the hollow fiber. In some embodiments, melting or sublimation used in combination with solvent dissolution or washing can clear a desired amount of solid core composition from the hollow fiber substantially faster than dissolution alone.

[00107] The removal of molten or sublimed species can be assisted by introducing a sweep liquid or gas to the bore of the fiber, e.g. to establish a convection current.

[00108] The removal of the core can be completed immediately after curing of the coating, or may be completed in a separate operation any time after the fiber has been produced. In some instances, it may be desirable to leave the core intact to provide additional support to the fiber during processing or otherwise assist in subsequent processing steps, such as module assembly. In some instances, it may be desirable to remove the core to assist in subsequent processing.

Coated core.

[00109] Various embodiments of the present invention provide a curable-composition coated core. The curable-composition coated core can be any suitable core consistent with the methods, cores, and curable compositions described herein. For example, in some embodiments, the present invention provides an organopolysiloxane-coated core. The coated core can include a solid substantially cylindrical core having a diameter of about 10 μm to about 2000 μm . The core can also include a core composition. The core composition can include about 50 wt% to about 100 wt% of a curable or sublimable composition that is at least one of meltable and sublimable at any suitable temperature, such as about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$. The coated core also can include a curable organopolysiloxane composition coated on the core. In some embodiments, the curable

composition coated on the core is at least partially cured.

[00110] Various embodiments of the present invention provide a cured curable-composition coated core. In some examples, the cured curable-composition includes a cured organopolysiloxane composition. The cured composition-coated core can include any suitable coated core consistent with the methods, cores, and curable compositions described herein. For example, in some embodiments, the present invention provides a core coated with a cured organopolysiloxane composition. The coated core can include a solid substantially cylindrical core having any suitable diameter, such as a diameter of about 10 μm to about 2000 μm . The core can include a core composition including about 50 wt% to about 100 wt% of a meltable or sublimable composition that is at least one of meltable and sublimable at any suitable temperature, such as at least one temperature between about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$. The coated core also includes an at least partially cured curable organopolysiloxane composition coated on the core. The walls of the at least partially cured organopolysiloxane composition can have any suitable thickness, such as a thickness of about 1 μm to about 200 μm . In some embodiments, the at least partially cured curable composition can be substantially fully cured.

Method of separating components in a feed mixture.

[00111] In various embodiments, the present invention provides a method of separating liquid or gas components in a feed gas or liquid mixture. The method of separating can be any suitable method of separating that includes a hollow fiber provided by any method described herein. In some examples, the method includes contacting a first side of a feed gas or liquid mixture with a membrane, wherein the membrane is a hollow fiber membrane generated by any method described herein. The feed mixture includes at least a first component and a second component. The contacting produces a permeate mixture on a second side of the membrane and a retentate mixture on the first side of the membrane. The permeate mixture is enriched in the first component, and the retentate mixture is depleted in the first component.

[00112] In some embodiments, the pressure on either side of the membrane can be about the same. In other embodiments, there can be a pressure differential between one side of the membrane and the other side of the membrane. For example, the pressure on the retentate side of the membrane can be higher than the pressure on the permeate side of the membrane. In other examples, the pressure on the permeate side of the membrane can be higher than the pressure on the retentate side of the membrane.

[00113] The feed gas mixture can include any mixture of gases or liquids. For example, the feed gas mixture can include hydrogen, carbon dioxide, nitrogen, ammonia, methane, water vapor, hydrogen sulfide, or any combination thereof. The feed gas or liquid can include any gas or liquid known to one of skill in the art. The membrane can be selectively

permeable to any one gas or liquid in the feed mixture, or to any of several gases or liquids in the feed mixture. The membrane can be selectively permeable to all but any one gas or liquid in the feed mixture.

[00114] Any number of membranes can be used to accomplish the separation. For

5 example, one membrane can be used, or a plurality of membranes can be used, such as in a hollow fiber module. In some embodiments, one or more hollow fibers provided by the method of the present invention are used in combination with other membranes, wherein the other membranes are any suitable membrane. The other membranes can be manufactured as flat sheets or as fibers and can be packaged into any suitable variety of
10 modules including hollow fibers, sheets or arrays of hollow fibers or sheets. Common module forms include hollow fiber modules, spiral wound modules, plate-and-frame modules, tubular modules and capillary fiber modules.

[00115] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to
15 the examples given herein.

Example 1. Curable organopolysiloxane.

[00116] A curable siloxane was prepared by combining 5.000 g of a siloxane-silsesquioxane blend (Blend 1) including 73 parts of dimethylvinylsiloxyl-terminated polydimethylsiloxane having a viscosity of about 55 Pa·s at 25° C and 27 parts of
20 organopolysiloxane resin including $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$ units, $(\text{CH}_3)_3\text{SiO}_{1/2}$ units, and $\text{SiO}_{4/2}$ units, wherein the mole ratio of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$ units and $(\text{CH}_3)_3\text{SiO}_{1/2}$ units combined to $\text{SiO}_{4/2}$ units is about 0.7, and the resin has weight-average molecular weight of about 22,000, a polydispersity of about 5, and contains about 1.8% by weight (about 5.5 mole %) of vinyl groups, and 0.1489 g of a polydimethylsiloxane-
25 polyhydridomethylsiloxane copolymer having an average viscosity of 0.03 Pa·s at 25 °C and including 1 wt % H in the form of SiH (Crosslinker 1) in a polypropylene cup and mixed in a counter-rotating centrifugal mixer at 2900 rpm for 30 s. The lid was removed and the side of the cup was scraped. The lid was replaced and the sample was mixed at 2900 rpm for 30s.

30 **[00117]** 1-Ethynyl-1-cyclohexanol was then added to the cup then mixed with two cycles at 2900 rpm for 30 s with a manual spatula mix in between. To the cup was then added 0.01 g a catalyst (Catalyst) including a mixture of 1% of a platinum(IV) complex of 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane, 92% of dimethylvinylsiloxyl-terminated polydimethylsiloxane having a viscosity of about 0.45 Pa·s at 25° C, and 7% of tetramethyldivinyldisiloxane and
35 mixed again in identical fashion. Lastly, 1.29 g hexane was added to the cup and mixed at 2900 rpm for 30 s.

Example 2. Coated core with polypropylene fiber support and D4 core composition.

[00118] A polypropylene support fiber having an outer diameter of 300 μm was threaded through a column of glassware that was designed for fiber coating. The fiber entered the bottom through a blunt tipped stainless steel syringe needle having an inner diameter of 413 μm into a reservoir containing liquid octamethylcyclotetrasiloxane (D4). The D4 coated fiber then was drawn through the center of a 19" tall double walled glass condenser that held liquid nitrogen. The fiber was cooled sufficiently while passing through the condenser to freeze the D4 around the fiber. The fiber then passed through a second blunt tipped stainless steel syringe needle of the same dimensions as the first into a pool of the curable siloxane composition described in Example 1. The fiber then continued through a die to remove excess coating before continuing through a 16 inch section of 3/8" stainless steel tubing wrapped with electric heat tape, which was heated to about 115 °C. The curable siloxane fully cured while travelling through this section of the apparatus. The finished fiber was then wound onto a spool attached to a motor that controlled the rate at which the fiber moved through the system. The fiber was drawn at speeds of 1 m/min and 2 m/min. Full cure of the siloxane coating was observed at both rates.

Example 3. Hollow fiber. (hypothetical example)

[00119] The frozen core of the sample drawn in Example 2 was allowed to melt at a temperature of 25 °C, and the polypropylene fiber was pulled out of the cured composition, yielding a hollow fiber.

Example 4. Coated core with polyvinyl alcohol (PVA) fiber support and D4 core composition.

[00120] The process described in Example 2 was repeated but the polypropylene fiber was substituted with a hollow polyvinyl alcohol (PVA) fiber having an outer diameter of about 200 μm as the support for the D4 frozen core. The first and second syringe needles in this case both had inner diameters of approximately 337 μm . The resulting fiber surface showed evidence of a cured siloxane coating at both line speeds of 1 m/min and 2 m/min.

Example 5. Hollow fiber. (hypothetical example)

[00121] The frozen D4 core in Example 4 was removed by thawing at 25 C and allowing the D4 to drain from the annular region between the cured coating and the PVA support fiber. This facilitated removal of the PVA fiber through dissolution with warm water, or by mechanical extraction, yielding a hollow fiber.

Example 6: Hollow fiber . (hypothetical example)

[00122] The D4 core in Example 4 was removed by removing the D4 after potting a series of fibers into a hollow fiber module using a polyurethane potting adhesive. The adhesive was allowed to cure at room temperature, then the interiors of the hollow fibers were exposed by cutting off the tip of the potted region. The D4 core was then removed by

pulling vacuum of approximately 50 Torr on the bores of the fibers at 25 C. This facilitated removal of the PVA support fiber through dissolution with warm water.

Example 6. Monofilament fiber support with aqueous core composition. (hypothetical example).

5 **[00123]** The procedure of Example 2 is followed, using a monofilament polyamide or polyester fiber in place of the polypropylene fiber, and using deionized water in place of D4. The sample is drawn at line speeds of 1 m/min and 2 m/min. Full cure of the siloxane coating occurs at both rates, and when inspected reveals a silicone hollow fiber from which the water-wettable fiber support could be extracted (after melting or sublimation of at least

10 part of the frozen water) to leave a free standing silicone hollow fiber membrane.

Example 7. Monofilament fiber support with hydrogel core composition. (hypothetical example).

[00124] The procedure of Example 2 is followed, using a monofilament polyamide or polyester fiber in place of the polypropylene fiber, and using an aqueous solution

15 containing 95 wt% deionized water and 5% of a water soluble polymer such as polyacrylic acid or gelatin that can form a hydrogel in place of the D4. The sample is drawn at line speeds of 1 m/min and 2 m/min. Full cure of the siloxane coating is observed at both rates, and when inspected revealed a silicone hollow fiber from which the frozen core could be melted or sublimed and the water-wettable fiber support could be extracted to leave a free

20 standing silicone hollow fiber membrane with a small residue of hydrogel containing polymer.

Example 8. Polypropylene fiber support with silicone and D4 core composition. (hypothetical example).

[00125] The procedure of Example 2 is followed, using 95% liquid D4 and 5 wt% of a

25 hydrosilylation curable silicone elastomer composition that together is capable of forming a gelled cyclosiloxane network in place of the D4. The sample is run at 1 m/min and 2 m/min. Full cure of the siloxane coating is observed at both rates, and when inspected reveal a silicone hollow fiber from which the frozen core could be melted or sublimed and the water-wettable fiber support could be extracted to leave a free standing silicone hollow

30 fiber membrane with a small residue of hydrogel containing polymer. The gelled D4 core could be removed under essentially identical conditions to un-gelled D4, but this approach can be performed without sub-ambient processing since the D4 behaves as a soft solid gel even at RT. Thus the D4 could be removed by heat or vacuum.

[00126] The terms and expressions which have been employed are used as terms of

35 description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the

invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments.

[00127] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[00128] Embodiment 1 provides a method of forming a hollow fiber, the method comprising: providing or obtaining a substantially cylindrical solid core comprising a core composition comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition; coating the core with a curable composition; curing the curable composition; melting or subliming at least part of the core composition; and removing at least part of the melted or sublimed part of the core composition, to provide a hollow fiber.

[00129] Embodiment 2 provides the method of Embodiment 1, wherein the core comprises at least one supporting fiber, wherein the core composition coats the supporting fiber.

[00130] Embodiment 3 provides the method of Embodiment 2, wherein providing or obtaining the core comprises: coating the supporting fiber with the core composition; and solidifying the core composition on the supporting fiber.

[00131] Embodiment 4 provides the method of any one of Embodiments 2-3, after melting or subliming at least part of the core composition, further comprising removing the supporting fiber from the hollow fiber.

[00132] Embodiment 5 provides the method of any one of Embodiments 2-4, wherein the supporting fiber comprises at least one of polypropylene, poly(vinyl alcohol), and monofilament water-wettable fiber.

[00133] Embodiment 6 provides the method of any one of Embodiments 2-5, wherein the supporting fiber has a diameter of about 10 μm to 600 μm .

[00134] Embodiment 7 provides the method of any one of Embodiments 1-6, wherein the core composition comprises at least one of water, an organocyclosiloxane, a hydrogel polymer, and a hydrosilylation curable silicone composition.

[00135] Embodiment 8 provides the method of Embodiment 7, wherein the organocyclosiloxane comprises about 3 to 12 di(C₁₋₅alkyl)siloxane repeating units.

[00136] Embodiment 9 provides the method of any one of Embodiments 7-8, wherein the core composition comprises less than about 20 wt% of the hydrogel polymer or less than about 20 wt% of the hydrosilylation curable silicone composition.

[00137] Embodiment 10 provides the method of any one of Embodiments 1-9, wherein the core composition comprises at least one of octamethylcyclotetrasiloxane, about 85 wt% to

99 wt% water and about 15 wt% to 1 wt% of the hydrogel polymer, and about 85 wt% to 99 wt% octamethylcyclotetrasiloxane and about 15 wt% to 1 wt% of a hydrosilylation curable silicone composition

[00138] Embodiment 11 provides the method of any one of Embodiments 1-10, wherein the core composition is more flowable than the cured curable composition at at least one temperature above the melting or sublimation point of the core composition.

[00139] Embodiment 12 provides the method of any one of Embodiments 1-11, wherein meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 °C to about 60 °C.

[00140] Embodiment 13 provides the method of any one of Embodiments 1-12, wherein at at least one temperature from about -100 °C to about 60 °C, the meltable or sublimable composition has a zero shear viscosity of about 100 cP or less.

[00141] Embodiment 14 provides the method of any one of Embodiments 1-13, wherein at about 25 °C the meltable or sublimable composition has a zero shear viscosity of about 100 cP or less.

[00142] Embodiment 15 provides the method of any one of Embodiments 1-14, wherein the curable composition comprises an organopolysiloxane.

[00143] Embodiment 16 provides the method of any one of Embodiments 1-15, wherein the curable composition comprises at least one of a hydrosilylation-curable composition, a condensation curable composition, a free-radical curable composition, an amine-epoxy curable composition, a radiation curable composition, a cooling-curable composition, or any combination thereof.

[00144] Embodiment 17 provides the method of any one of Embodiments 1-16, wherein the core is substantially cylindrical.

[00145] Embodiment 18 provides the method of any one of Embodiments 1-17, wherein the core has a diameter of about 10 µm to about 2000 µm.

[00146] Embodiment 19 provides the method of any one of Embodiments 1-18, wherein curing comprises hydrosilylation curing, condensation curing, free-radical curing, amine-epoxy curing, radiation curing, cooling, or any combination thereof.

[00147] Embodiment 20 provides the method of any one of Embodiments 1-19, wherein the hollow fiber comprises walls having a thickness of about 1 µm to 200 µm.

[00148] Embodiment 21 provides the method of any one of Embodiments 1-20, wherein the method is continuous.

[00149] Embodiment 22 provides a hollow fiber made using the method of any one of Embodiments 1-21.

[00150] Embodiment 23 provides a method of forming a silicone hollow fiber, the method comprising: providing or obtaining a substantially cylindrical solid core having a diameter of

about 100 μm to about 500 μm , the core comprising at least one supporting fiber and a core composition coating the supporting fiber comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition, wherein the meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$; coating
5 the core with a curable composition comprising an organopolysiloxane; curing the curable composition; melting or subliming at least part of the core composition; and removing at least part of the melted or sublimed part of the core composition, to provide a silicone hollow fiber comprising walls with a thickness of about 10 μm to about 60 μm .

[00151] Embodiment 24 provides a method of forming a silicone hollow fiber, the method
10 comprising: providing or obtaining a substantially cylindrical solid core having a diameter of about 100 μm to about 500 μm , the core comprising a core composition comprising about 50 wt% to about 100 wt% of a composition that has a zero shear viscosity of about 100 cP or less at at least one temperature of 0 $^{\circ}$ C to 60 $^{\circ}$ C; coating the core with a curable composition comprising an organopolysiloxane; curing the curable composition; melting or
15 subliming at least part of the core composition; and removing at least part of the melted or sublimed part of the core composition, to provide a silicone hollow fiber comprising walls with a thickness of about 10 μm to about 60 μm .

[00152] Embodiment 25 provides an organopolysiloxane-coated core comprising: a solid substantially cylindrical core having a diameter of about 10 μm to about 2000 μm , the core
20 comprising a core composition comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition, wherein the meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$; a curable composition coated on the core, the curable composition comprising an organopolysiloxane.

[00153] Embodiment 26 provides the coated core of Embodiment 25, wherein the curable composition coated on the core is at least partially cured.

[00154] Embodiment 27 provides a core coated with a cured organopolysiloxane composition, the coated core comprising: a solid substantially cylindrical core having a diameter of about 10 μm to about 2000 μm , the core comprising a core composition
30 comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition, wherein the meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 $^{\circ}\text{C}$ to about 60 $^{\circ}\text{C}$; an at least partially cured curable composition coated on the core, the curable composition comprising an organopolysiloxane and comprising walls having a thickness of about 1 μm to about 200
35 μm .

[00155] Embodiment 28 provides a method of separating components in a feed mixture, the method comprising: contacting a first side of a membrane with a feed gas or liquid

mixture comprising at least a first component and a second component to produce a permeate mixture on a second side of the membrane and a retentate mixture on the first side of the membrane, wherein the permeate mixture is enriched in the first component, and the retentate mixture is depleted in the first component; wherein the membrane
5 comprises the hollow fiber provided by the method of any one of Embodiments 1-24.

[00156] Embodiment 29 provides the apparatus or method of any one or any combination of Embodiments 1-28 optionally configured such that all elements or options recited are available to use or select from.

CLAIMS

What is claimed is:

1. A method of forming a hollow fiber, the method comprising:
providing or obtaining a substantially cylindrical solid core comprising a core composition comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition;
coating the core with a curable composition;
curing the curable composition;
melting or subliming at least part of the core composition; and
removing at least part of the melted or sublimed part of the core composition, to provide a hollow fiber.
2. The method of claim 1, wherein the core comprises at least one supporting fiber, wherein the core composition coats the supporting fiber.
3. The method of claim 2, wherein providing or obtaining the core comprises:
coating the supporting fiber with the core composition; and
solidifying the core composition on the supporting fiber.
4. The method of any one of claims 2-3, after melting or subliming at least part of the core composition, further comprising removing the supporting fiber from the hollow fiber.
5. The method of any one of claims 2-4, wherein the supporting fiber comprises at least one of polypropylene, poly(vinyl alcohol), and monofilament water-wettable fiber.
6. The method of any one of claims 1-5, wherein the core composition comprises at least one of water, an organocyclosiloxane, a hydrogel polymer, and a hydrosilylation curable silicone composition.
7. The method of any one of claims 1-6, wherein the core composition is more flowable than the cured curable composition at at least one temperature above the melting or sublimation point of the core composition.
8. The method of any one of claims 1-7, wherein meltable or sublimable composition is meltable or sublimable at at least one temperature of about -200 °C to about 60 °C.

9. The method of any one of claims 1-8, wherein at at least one temperature from about -100 °C to about 60 °C, the meltable or sublimable composition has a zero shear viscosity of about 100 cP or less.
10. The method of any one of claims 1-9, wherein at about 25 °C the meltable or sublimable composition has a zero shear viscosity of about 100 cP or less.
11. The method of any one of claims 1-10, wherein the curable composition comprises an organopolysiloxane.
12. The method of any one of claims 1-11, wherein the core has a diameter of about 10 µm to about 2000 µm.
13. The method of any one of claims 1-12, wherein the hollow fiber comprises walls having a thickness of about 1 µm to 200 µm.
14. A method of forming a silicone hollow fiber, the method comprising:
providing or obtaining a substantially cylindrical solid core having a diameter of about 100 µm to about 500 µm, the core comprising at least one supporting fiber and a core composition coating the supporting fiber comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition, wherein the meltable or sublimable composition is at least one of
meltable or sublimable at at least one temperature of about -200 °C to about 60 °C, and
has a zero shear viscosity of about 100 cP or less at at least one temperature of 0° C to 60° C;
coating the core with a curable composition comprising an organopolysiloxane;
curing the curable composition; melting or subliming at least part of the core composition; and
removing at least part of the melted or sublimed part of the core composition, to provide a silicone hollow fiber comprising walls with a thickness of about 10 µm to about 60 µm.
15. An organopolysiloxane-coated core comprising:
a solid substantially cylindrical core having a diameter of about 10 µm to about 2000 µm, the core comprising a core composition comprising about 50 wt% to about 100 wt% of a meltable or sublimable composition, wherein the meltable or sublimable

composition is meltable or sublimable at at least one temperature of about -200 °C to about 60 °C;

a curable composition coated on the core, the curable composition comprising an organopolysiloxane.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/024357

A. CLASSIFICATION OF SUBJECT MATTER

INV. D01D5/24 B01D63/02 D06M15/643 D01F9/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D01D B01D D06M C08L D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2004/197557 A1 (ESHRAGHI RAY R [US] ET AL) 7 October 2004 (2004-10-07) abstract; claims 1,2; figures 1-8 paragraphs [0105] - [0138] -----	1-5,7, 12,13 6,8,14, 15
X A	US 2012/128978 A1 (BALLWEG THOMAS [DE] ET AL) 24 May 2012 (2012-05-24) abstract; claims 1,2,13,14,16,17; figures 1-3 -----	1,6,7, 11-13 8-10,14, 15
X	US 2003/026985 A1 (GREINER ANDREAS [DE] ET AL) 6 February 2003 (2003-02-06) claims 3,8; example 5 figure 1; examples 1-4 -----	1,7,11
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Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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