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(54) **Title:** METHOD OF RECYCLING SILICONE WASTE WITH THE USE OF ORGANIC POLYMER AND DEPOLYMERIZATION CATALYST

(57) **Abstract:** A method that includes: (a) heating a mixture that includes: (i) silicone, (ii) an organic polymer, and (iii) a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide heated mixture comprising a cyclosiloxane and a residue. The method also optionally further includes (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane, (c) forming an extrudate from the residue; and (d) heating the extrudate, sufficient to depolymerize at least a portion of remaining silicone located therein.



**METHOD OF RECYCLING SILICONE WASTE
WITH THE USE OF ORGANIC POLYMER AND
DEPOLYMERIZATION CATALYST**

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/768,710, filed on February 25, 2013, the entire disclosure of which is incorporated by reference as if fully set forth herein.

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BRIEF SUMMARY OF THE INVENTION

The present invention provides a method that includes: (a) heating a mixture that includes: (i) silicone, (ii) an organic polymer, and (iii) a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide heated mixture comprising a cyclosiloxane and a residue. The method also includes (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane.

The present invention also provides a method for recycling a silicone waste. The method includes: (a) heating a mixture that includes (i) a silicone waste, (ii) an organic polymer, and (iii) a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone waste, to provide a heated mixture comprising cyclosiloxane and a residue. The method also includes: (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane, (c) forming an extrudate from the residue; and (d) heating the extrudate, sufficient to depolymerize at least a portion of remaining silicone waste located therein.

In specific embodiments, advantages of the invention include the catalytic depolymerization of silicone waste to cyclosiloxanes, in a continuous manner. In additional specific embodiments, advantages of the invention include the catalytic depolymerization of silicone waste to cyclosiloxanes, at a relatively high conversion. In specific embodiments, advantages of the invention include the catalytic depolymerization of silicone waste to cyclosiloxanes, in a continuous manner with very good process stability at high conversion. In additional specific embodiments, advantages of the invention include the catalytic depolymerization of silicone waste to cyclosiloxanes, at a relatively low

temperature. In additional specific embodiments, advantages of the invention include the catalytic depolymerization of a relatively diverse and broad array of silicone waste, to cyclosiloxanes. Specifically, the silicone waste to be depolymerized can vary with respect to the physical form and/or chemical reactivity. In additional specific embodiments, advantages of the invention include the catalytic depolymerization of silicone waste carried out in the presence of an organic thermoplastic polymer (e.g., polyolefin). In additional specific embodiments, advantages of the invention include the recycling of an organic polymer (e.g., thermoplastic waste, such as a polyolefin). Specifically, the method described herein employs an organic polymer, in addition to a depolymerization catalyst, to provide a cyclosiloxane and a residue. The organic polymer can be a waste product, suitable for recycling.

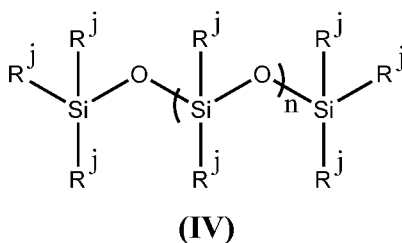
DETAILED DESCRIPTION

The following detailed description includes embodiments and examples, in which the invention may be practiced. These embodiments and examples are described in enough detail to enable those skilled in the art to practice the invention. The embodiments may be combined, other embodiments may be utilized, or structural, and logical changes may be made without departing from the scope of the present invention. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined by the appended claims and their equivalents.

Definitions

As used herein, “silicone,” “siloxane,” “polysilicone,” “polysiloxane,” “polymerized silicone,” or “polymerized siloxane” refers to a mixed inorganic-organic polymer that includes an Si-O-Si backbone. For example, the silicone polymer can be a linear polymer (e.g., volatile and nonvolatile fluids such as dimethicone), a ring polymer (e.g., volatile fluids such as cyclomethicone), a branched polymer, a crosslinked polymer (e.g. gels, elastomers, sealants, and rubber), or a resin (e.g., structures that cure to create three-dimensional films).

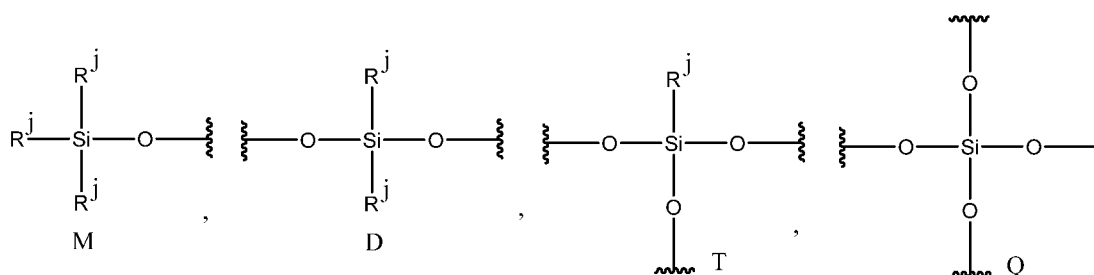
In specific embodiments, the silicone can be a compound of formula (IV):



wherein,

- each R^j is independently at each occurrence an organic group, such as,
 5 e.g., methyl, ethyl, or phenyl, optionally substituted; and
 n is a whole integer greater than 1.

The main chain unit, $-(\text{SiR}^j\text{R}^j\text{O})-$, is often shortened by the letter D because, as the silicon atom is connected with two oxygen atoms, this unit is capable of expanding within the polymer in two directions. In a similar way, M
 10 (trialkyl-), T (monoalkyl-), and Q (no alkyl) units can be defined corresponding to:



15 wherein,

each R^j is independently an organic group, such as, e.g., methyl, ethyl, or phenyl, optionally substituted.

As such, in specific embodiments, the present invention includes M, D, Q and T silicone polymers as described above.

20 These polymers consist of an inorganic silicon-oxygen backbone ($\cdots\text{Si-O-Si-O-Si-O}\cdots$), with organic side groups attached to each of the silicon atoms, which are four-coordinate. In some cases, organic side groups can be used to link two or more of these $-\text{Si-O}-$ backbones together. By varying the

$-\text{Si-O}-$ chain lengths, side groups, and crosslinking, silicones can be
 25 synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The siloxane can be, e.g., linear polydimethylsiloxane (PDMS).

As used herein, "silicone material" refers to a material that includes silicone. The silicone can be present, e.g., in at least about 0.1 wt.% of the silicone material. Additionally, the silicone can be present, e.g., in up to about 100 wt.% of the silicone material.

- 5 As used herein, "hydrocarbyl" refers to a hydrocarbon in which a hydrogen atom is removed. As such, it is derived from an organic compound, and consists of hydrogen and carbon atoms, wherein the carbon atoms are optionally substituted, e.g., with one or more halo.

Silicone material

- 10 The method described herein includes heating a mixture that includes silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a cyclosiloxane and a residue. As such, the method described herein produces depolymerized material from a silicone material. In specific embodiments, the
15 depolymerized material is produced via a de-polymerization of silicone waste material, thereby recycling the silicone waste material.

- Any suitable silicone material can be employed, provided the depolymerized material is produced. For example, the silicone material can include solid silicones, liquid silicones, dispersions of silicones, a mixture of
20 silicones with organic and inorganic compounds, or a combination thereof. In specific embodiments, the silicone material includes an organopolysiloxane. In additional specific embodiments, the silicone material includes an organopolysiloxane having silicon-bonded groups independently selected from hydrocarbyl.

- 25 In additional specific embodiments, the silicone material includes at least one of a silicone liquid, a silicone fluid, a silicone gum, a silicone gel, a silicone solid, a silicone resin, a cured silicone polymer, an uncured silicone gum, a silicone emulsion, a silicone sealant, a silicone rubber, a silicone oil, a silicone grease, a silicone tubing, liquid silicone rubber, a silicone elastomer, a silicone
30 band, a silicone tubing, a filled silicone polymer, a fiber reinforced silicone polymer, a silicone sheet, a silicone mat, a silicone varnish, and a silicone glove.

In additional specific embodiments, the silicone material includes at least one of polydimethylsiloxane (PDMS), polymethylhydrogensiloxane,

polymethylvinylsiloxane, polydiethylsiloxane, polymethylethylsiloxane, phenylmethyl silicone, and fluoroalkylsilicone.

In additional specific embodiments, the silicone material includes silicone polymers terminated with at least one of trimethylsiloxy, vinyl dimethylsiloxy, dimethylphenylsiloxy, diphenylmethylsiloxy, dimethylhydroxylsiloxy, chlorodimethylsiloxy, chloromethyldimethylsiloxy, ethyldimethylsiloxy, propyldimethylsiloxy, allyldimethylsiloxy, and hydrogendimethylsiloxy.

The silicone can be present in the silicone material, in any suitable amount. For example, the silicone can be present in about 0.1 wt.% to about 100 wt.% of the silicone material. Likewise, the silicone can be present in the mixture, in any suitable amount. For example, the silicone can be present in at least about 0.1 wt.% of the mixture. Additionally, the silicone can be present in up to about 99 wt.% of the mixture. In specific embodiments, the silicone is present in about 1 wt.% to about 99 wt.% of the mixture.

In additional specific embodiments, the silicone is present in at least about 1 wt.% of the mixture. In additional specific embodiments, the silicone is present in at least about 10 wt.% of the mixture. In additional specific embodiments, the silicone is present in at least about 25 wt.% of the mixture. In additional specific embodiments, the silicone is present in at least about 50 wt.% of the mixture. In additional specific embodiments, the silicone is present in at least about 75 wt.% of the mixture. In additional specific embodiments, the silicone is present in at least about 90 wt.% of the mixture.

In additional specific embodiments, the silicone is present in up to about 98 wt.% of the mixture. In additional specific embodiments, the silicone is present in up to about 97 wt.% of the mixture. In additional specific embodiments, the silicone is present in up to about 96 wt.% of the mixture. In additional specific embodiments, the silicone is present in up to about 95 wt.% of the mixture. In additional specific embodiments, the silicone is present in up to about 90 wt.% of the mixture.

In additional specific embodiments, the silicone is present in about 10 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 20 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 30 wt.% to

about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 40 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 50 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 60 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 70 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the silicone is present in about 80 wt.% to about 99 wt.% of the mixture.

Any suitable amount of silicone can be depolymerized, employing the method described herein. In specific embodiments, at least about 50 wt.% of the silicone is depolymerized, employing the method described herein. In additional specific embodiments, at least about 75 wt.% of the silicone is depolymerized, employing the method described herein. In additional specific embodiments, at least about 90 wt.% of the silicone is depolymerized, employing the method described herein. In additional specific embodiments, at least about 95 wt.% of the silicone is depolymerized, employing the method described herein. In additional specific embodiments, at least about 98 wt.% of the silicone is depolymerized, employing the method described herein. In additional specific embodiments, up to about 100 wt.% of the silicone is depolymerized, employing the method described herein.

Organic polymer

The method described herein employs an organic polymer, in addition to a depolymerization catalyst, to provide a cyclosiloxane and a residue. In specific embodiments, the organic polymer can be a waste product, suitable for recycling.

In specific embodiments, the organic polymer is a thermoplastic organic polymer. In additional specific embodiments, the organic polymer is a polyolefin.

In specific embodiments, the organic polymer includes at least one of a straight-chain polyolefin or copolymer polyolefin, a branched polyolefin or copolymer polyolefin, a grafted polyolefin or copolymer polyolefin, a borane-grafted polyolefin, a polyolefin with side hydroxyl group, a polyolefin grafted with another polymer, a blend of polyolefin with another polymer, and a polyolefin filled with an inorganic material.

In specific embodiments, the organic polymer includes at least one of polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), polyisobutylene, poly(ethylene-co-propylene), poly(propylene-co-1,4-hexadiene), poly(isobutylene-co-isoprene), poly(ethylene-co-propylene-co-1,4-hexadiene), PE-g-PVA, PP-g-PMMA, PP-g-PVA, PE-g-PCL, PP-g-PCL, EP-g-PMMA, butyl-g-PMMA, PMMA, PVA, PS, PVC, PVAC, and a polyolefin filled with at least one of mica, calcium carbonate, silica, glass, magnesium oxide, aluminum oxide, and clay.

In specific embodiments, the organic polymer is a thermoplastic organic polymer that includes at least one of low density polyethylene (LDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE).

In specific embodiments, the organic polymer is a thermoplastic organic polymer that includes at least one of polyoxymethylene, polyoxymethylene copolymer with oxyethylene and others structural units, polymethylmethacrylate (PMMA), PMMA copolymers, polystyrene, polystyrene copolymers, celluloid, celluloid acetate, cyclic olefin copolymers, ethylene-vinyl acetate (EVA), ethylene-vinyl alcohol (EVOH), fluoroplastics, PTFE, acrylonitrile-butadiene-styrene (ABS), polyacrylates, polyamides, polyamide-imide, polyimides, polyetherimide, polysulfones, polyethersulfones, polyketones, polyetheretherketone (PEEK), polycarbonate, polyesters, polycaprolactone, polybutylene terephthalate, polyethylene terephthalate, polylactic acid, polyphenylene oxide, polyphenylene sulfide, thermoplastic polyurethane, polyvinylacetate (PVA), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), and styrene-acrylonitrile (SAN) copolymer.

The organic polymer can be present in the mixture, in any suitable amount. For example, the organic polymer can be present in about 0.1 wt.% to about 99 wt.% of the mixture. Additionally, the organic polymer can be present in up to about 99 wt.% of the mixture. In specific embodiments, the organic polymer is present in about 1 wt.% to about 99 wt.% of the mixture.

In additional specific embodiments, the organic polymer is present in at least about 1 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in at least about 5 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in at least about 10 wt.% of the mixture. In additional specific embodiments, the organic polymer is

present in at least about 15 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in at least about 20 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in at least about 25 wt.% of the mixture.

5 In additional specific embodiments, the organic polymer is present in up to about 98 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in up to about 97 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in up to about 96 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in
10 up to about 95 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in up to about 90 wt.% of the mixture.

 In additional specific embodiments, the organic polymer is present in about 1 wt.% to about 99 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in about 1 wt.% to about 75 wt.%
15 of the mixture. In additional specific embodiments, the organic polymer is present in about 1 wt.% to about 50 wt.% of the mixture. In additional specific embodiments, the organic polymer is present in about 1 wt.% to about 25 wt.% of the mixture.

Depolymerization catalyst

20 The method described herein employs a depolymerization catalyst, in addition to an organic polymer, to provide a cyclosiloxane and a residue.

 The methods described herein employ a depolymerization catalyst, in addition to an organic polymer, to produce a depolymerized material from a silicone material.

25 In specific embodiments, the depolymerization catalyst includes an organic base. In additional specific embodiments, the depolymerization catalyst includes an inorganic base.

 In specific embodiments, the depolymerization catalyst includes an organic acid. In additional specific embodiments, the depolymerization catalyst
30 includes an inorganic acid.

 In additional specific embodiments, the depolymerization catalyst includes a solid acid selected from at least one of aluminosilicates, acid treated aluminosilicates, zeolites, mixed metal oxides, heteropolyacids, sulfated metal

oxides, carbon based solid acids, ion exchange resins, sulfonated polymers, high molecular weight carboxylic acids, and acidic metal salts.

In additional specific embodiments, the depolymerization catalyst includes at least one of a clay, a mixed metal oxide, and a sulfonated metal
5 oxide.

In additional specific embodiments, the depolymerization catalyst includes at least one of kaolin, smectite, illite, chlorites, and palygorskitem sepiolite.

In additional specific embodiments, the depolymerization catalyst
10 includes at least one of montmorillonite, saponite, nontronite (ironsmectite), beidellite, bentonite, and hectorite.

In additional specific embodiments, the depolymerization catalyst includes a clay. In additional specific embodiments, the depolymerization catalyst includes an acid-washed clay.

15 The depolymerization catalyst can be present in the mixture, in any suitable amount. For example, the depolymerization catalyst can be present in about 0.01 wt.% to about 25 wt.% of the mixture. In specific embodiments, the depolymerization catalyst is present in about 0.01 wt.% to about 25 wt.% of the mixture. In additional specific embodiments, the depolymerization catalyst is
20 present in about 0.05 wt.% to about 25 wt.% of the mixture. In additional specific embodiments, the depolymerization catalyst is present in about 0.01 wt.% to about 20 wt.% of the mixture. In additional specific embodiments, the depolymerization catalyst is present in about 0.01 wt.% to about 15 wt.% of the mixture. In additional specific embodiments, the depolymerization catalyst is
25 present in about 0.01 wt.% to about 10 wt.% of the mixture.

Organic solvent

The method described herein includes heating a mixture that includes silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide
30 a cyclosiloxane and a residue. In specific embodiments, the mixture will include no appreciable or significant amount of organic solvent.

In additional specific embodiments, the heated mixture will include less than about 20 wt.% organic solvent. In additional specific embodiments, the heated mixture will include less than about 10 wt.% organic solvent. In specific

embodiments, the mixture will include less than about 1 wt.% organic solvent. In additional specific embodiments, the mixture will include less than about 0.5 wt.% organic solvent. In specific embodiments, the mixture will include less than about 0.1 wt.% organic solvent. In specific embodiments, the mixture will include less than about 0.05 wt.% organic solvent.

Prior to the heating, each of the silicone, organic polymer and depolymerization catalyst can be contacted to provide a mixture. Additionally, each of these components can be mixed together to provide a mixture that is relatively homogeneous. The contacting and/or mixing can be carried out in any suitable manner and employing any suitable device. For example, each of the silicone, organic polymer and depolymerization catalyst can be mixed together, employing at least one of a high shear mechanical device, an extruder, and a twin-screw extruder, equipped with degassing ports.

Filler

The method described herein includes heating a mixture that includes silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a cyclosiloxane and a residue. In specific embodiments, the mixture will include additional substances, such as, e.g., a filler. For example, the mixture can further include at least one of silica, calcium carbonate, and alumina.

Heating

The method described herein includes heating a mixture that includes silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a cyclosiloxane and a residue. The heating can be carried out under any suitable conditions sufficient to depolymerize at least a portion of the silicone, to provide a cyclosiloxane and a residue.

In specific embodiments, the heating is carried out for at least about 0.1 minute. In additional specific embodiments, the heating is carried out for at least about 1 minute. In additional specific embodiments, the heating is carried out for at least about 5 minutes. In additional specific embodiments, the heating is carried out for at least about 10 minutes. In additional specific embodiments, the heating is carried out for at least about 30 minutes. In additional specific embodiments, the heating is carried out for at least about 1 hour.

In specific embodiments, the heating is carried out for up to about 24 hours. In specific embodiments, the heating is carried out for up to about 12 hours. In additional specific embodiments, the heating is carried out for up to about 8 hours. In additional specific embodiments, the heating is carried out for up to about 6 hours. In additional specific embodiments, the heating is carried out for up to about 4.5 hours.

In specific embodiments, the heating is carried out for about 0.1 minute to about 24 hours. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 2 hours. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 1 hours. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 30 minutes. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 15 minutes. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 10 minutes. In additional specific embodiments, the heating is carried out for about 0.1 minute to about 5 minutes. In additional specific embodiments, the heating is carried out for about 1 hour to about 24 hours. In additional specific embodiments, the heating is carried out for about 1 hour to about 12 hours. In additional specific embodiments, the heating is carried out for about 1 hour to about 8 hours. In additional specific embodiments, the heating is carried out for about 1 hour to about 6 hours. In additional specific embodiments, the heating is carried out for about 1 hour to about 4.5 hours.

In specific embodiments, the heating is carried out such that the temperature of the mixture is below the decomposition temperature of the organic polymer. In additional specific embodiments, the heating is carried out such that the temperature of the mixture is at least about 5°C below the decomposition temperature of the organic polymer. In additional specific embodiments, the heating is carried out such that the temperature of the mixture is at least about 10°C below the decomposition temperature of the organic polymer.

In specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 60°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 90°C. In additional specific embodiments, the heating is carried out such

that the mixture reaches a temperature of at least about 120°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 150°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 180°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 210°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of at least about 240°C.

In specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 330°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 320°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 310°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 300°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 290°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature below about 280°C.

In specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 60°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 90°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 120°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 150°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 180°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 210°C to about 340°C. In additional specific embodiments, the heating is carried out such that the mixture reaches a temperature of about 240°C to about 340°C. The upper temperature limit is typically determined by

the decomposition temperatures of the silicone and more importantly of the organic polymer.

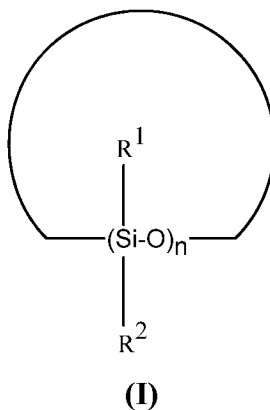
In specific embodiments, the heating is carried out in a batch mode. In additional specific embodiments, the heating is carried out in a continuous fashion.

The heating can be carried out in any suitable manner employing any suitable heating device. For example, the heating can be carried out with devices such as a pyrolysis kiln, a fluidized bed reactor, and/or a twin-screw extruder, equipped with degassing ports.

10 Cyclosiloxane

The method described herein includes heating a mixture that includes silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a cyclosiloxane and a residue.

15 In specific embodiments, the cyclosiloxane includes a compound of formula (I):



wherein,

20 each of R¹ - R² is independently hydrogen, (C₁-C₁₂) alkyl, (C₆-C₁₂) aryl, (C₆-C₁₂) aryl (C₁-C₁₂) alkyl, or (C₁-C₁₂) alkyl (C₆-C₁₂) aryl, optionally substituted with one or more halo; and

n is a whole integer from about 3 to about 20.

In specific embodiments, each of R¹ and R² is hydrogen, (C₁-C₁₂) alkyl, (C₆-C₁₂) aryl, (C₆-C₁₂) aryl (C₁-C₁₂) alkyl, or (C₁-C₁₂) alkyl (C₆-C₁₂) aryl, optionally substituted with one or more halo.

In specific embodiments, each of R¹ and R² is (C₁-C₁₂) alkyl.

In specific embodiments, each of R¹ and R² is methyl.

In specific embodiments, n is at least about 3.

In specific embodiments, n is up to about 7.

In specific embodiments, n is up to about 20.

5 In specific embodiments, n is up to about 25.

In specific embodiments, n is about 3 to about 7.

In specific embodiments, n is 3. In additional specific embodiments, n is 4. In additional specific embodiments, n is 5. In additional specific embodiments, n is 6. In additional specific embodiments, n is 7. In specific
10 embodiments, the cyclosilane is a mixture of cyclosiloxanes with n ranging from 3 to 12.

In addition to the cyclic siloxane, the depolymerized material can optionally further include an acyclic siloxane oligomer/monomer or a linear siloxane oligomer/monomer. Specifically, the acyclic siloxane
15 oligomer/monomer can include one or more (e.g., 2, 3, 4, etc.) acyclic siloxane oligomers/monomers.

The depolymerized material or crude cyclosiloxane can optionally be subsequently purified. The cyclosiloxane (crude or purified) can be offered as a commercial product. Alternatively, the cyclosiloxane (crude or purified) can
20 optionally be subsequently polymerized to a polysiloxane.

Degassing

The method described herein includes degassing the heated mixture, to remove at least a portion of the cyclosiloxane, and to collect the condensed vapor as products. The degassing can be carried out under any suitable
25 conditions sufficient to remove at least a portion of the cyclosiloxane.

In specific embodiments, the degassing is carried out by applying a vacuum to the heated mixture. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of less than about 500 mm Hg. In more specific embodiments, the degassing is carried out by applying
30 to the heated mixture a vacuum of less than about 400 mm Hg. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of less than about 300 mm Hg. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of less than

about 200 mm Hg. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of less than about 100 mm Hg.

In specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 500 mm Hg. In more
5 specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 400 mm Hg. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 300 mm Hg. In more specific
10 embodiments, the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 200 mm Hg. In more specific embodiments, the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 100 mm Hg. Degassing can also be accomplished by applying a vacuum of less than 35 mm Hg.

In specific embodiments, the heated mixture will include no appreciable
15 or significant amount of organic solvent. In additional specific embodiments, the heated mixture will include less than about 20 wt.% organic solvent. In additional specific embodiments, the heated mixture will include less than about 10 wt.% organic solvent. In additional specific embodiments, the heated mixture will include less than about 1 wt.% organic solvent. In additional specific
20 embodiments, the heated mixture will include less than about 0.5 wt.% organic solvent. In additional specific embodiments, the heated mixture will include less than about 0.1 wt.% organic solvent. In additional specific embodiments, the heated mixture will include less than about 0.05 wt.% organic solvent.

In specific embodiments, the degassing is carried out in a batch mode. In
25 additional specific embodiments, the degassing is carried out in a continuous fashion.

Extrudate

The method disclosed herein can optionally further include forming an extrudate from the residue. When an extrudate is formed from the residue, the
30 method disclosed herein can optionally further include heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone located therein. When performed, the heating of the extrudate can be carried out under any suitable conditions, sufficient to depolymerize at least a portion of remaining

silicone located therein. For example, when performed, the heating of the extrudate can be carried out in a pyrolysis kiln or fluidized bed.

In specific embodiments, the heating of the extrudate is carried out at a temperature below the decomposition temperature of the organic polymer. In
5 additional specific embodiments, the heating of the extrudate is carried out at such that the extrudate reaches a temperature of at least about 120°C. In additional specific embodiments, the heating of the extrudate is carried out at such that the extrudate reaches a temperature below about 340°C. In additional
10 specific embodiments, the heating of the extrudate is carried out at such that the extrudate reaches a temperature of about 120°C to about 340°C.

In specific embodiments, at least about 1 wt.% of the remaining silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 10 wt.% of the remaining silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 25 wt.% of the
15 remaining silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 50 wt.% of the remaining silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 70 wt.% of the remaining silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 90 wt.% of the remaining
20 silicone (from the extrudate) is depolymerized. In additional specific embodiments, at least about 95 wt.% of the remaining silicone (from the extrudate) is depolymerized.

Enumerated Embodiments

Specific enumerated embodiments [1] to [73] provided below are for
25 illustration purposes only, and do not otherwise limit the scope of the disclosed subject matter, as defined by the embodiments. These enumerated embodiments encompass all combinations, sub-combinations, and multiply referenced (e.g., multiply dependent) combinations described therein.

1. A method comprising: (a) heating a mixture comprising a
30 silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a heated mixture comprising cyclosiloxane and a residue; and (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane.

2. The method of the above embodiment, which is a method for recycling silicone.

3. The method of any one of the above embodiments, wherein the silicone is waste.

5 4. The method of any one of the above embodiments, wherein the silicone comprises solid silicones, liquid silicones, dispersions of silicones, a mixture of silicones with organic and inorganic compounds, or a combination thereof.

5. The method of any one of the above embodiments, wherein the
10 silicone comprises at least one of a silicone liquid, a silicone fluid, a silicone gum, a silicone gel, a silicone solid, a silicone resin, a cured silicone polymer, an uncured silicone gum, a silicone emulsion, a silicone sealant, a silicone rubber, a silicone oil, a silicone grease, a silicone tubing, liquid silicone rubber, a silicone elastomer, a silicone band, a silicone tubing, a filled silicone polymer, a fiber
15 reinforced silicone polymer, a silicone sheet, a silicone mat, a silicone varnish, and a silicone glove.

6. The method of any one of the above embodiments, wherein the silicone comprises an organopolysiloxane.

7. The method of any one of the above embodiments, wherein the
20 silicone comprises an organopolysiloxane having silicon-bonded groups independently selected from hydrocarbyl.

8. The method of any one of the above embodiments, wherein the silicone comprises at least one of polydimethylsiloxane (PDMS), polymethylhydrogensiloxane, polymethylvinylsiloxane, polydiethylsiloxane,
25 polymethylethylsiloxane, phenylmethyl silicone, and fluoroalkylsilicone.

9. The method of any one of the above embodiments, wherein the silicone comprises silicone polymers terminated with at least one of trimethylsiloxy, vinyltrimethylsiloxy, dimethylphenylsiloxy, diphenylmethylsiloxy, dimethylhydroxysiloxy, chlorodimethylsiloxy,
30 chloromethyltrimethylsiloxy, ethyltrimethylsiloxy, propyltrimethylsiloxy, allyltrimethylsiloxy, and hydrogendimethylsiloxy.

10. The method of any one of the above embodiments, wherein the silicone is present in about 1 wt.% to about 99 wt.% of the mixture.

11. The method of any one of the above embodiments, wherein the silicone is present in about 50 wt.% to about 99 wt.% of the mixture.

12. The method of any one of the above embodiments, wherein the organic polymer is a thermoplastic organic polymer.

5 13. The method of any one of the above embodiments, wherein the organic polymer comprises a polyolefin.

14. The method of any one of the above embodiments, wherein the organic polymer comprises at least one of a straight-chain polyolefin or copolymer polyolefin, a branched polyolefin or copolymer polyolefin, a grafted
10 polyolefin or copolymer polyolefin, a borane grafted polyolefin, a polyolefin with side hydroxyl group, a polyolefin grafted with another polymer, a blend of polyolefin with another polymer, and a polyolefin filled with an inorganic material.

15. The method of any one of the above embodiments, wherein the
15 organic polymer comprises at least one of polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), polyisobutylene, poly(ethylene-co-propylene), poly(propylene-co-1,4-hexadiene), poly(isobutylene-co-isoprene), poly(ethylene-co-propylene-co-1,4-hexadiene, PE-g-PVA, PP-g-PMMA, PP-g-PVA, PE-g-PCL, PP-g-PCL, EP-g-PMMA,
20 butyl-g-PMMA, PMMA, PVA, PS, PVC, PVAC, and a polyolefin filled with at least one of mica, calcium carbonate, silica, glass, magnesium oxide, aluminum oxide, and clay.

16. The method of any one of the above embodiments, wherein the organic polymer is a thermoplastic organic polymer comprising at least one of
25 low density polyethylene (LDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE).

17. The method of any one of the above embodiments, wherein the organic polymer is a thermoplastic organic polymer comprising at least one of
30 polyoxymethylene, polyoxymethylene copolymer with oxyethylene and others structural units, polymethylmethacrylate (PMMA), PMMA copolymers, polystyrene, polystyrene copolymers, celluloid, celluloid acetate, cyclic olefin copolymers, ethylene-vinyl acetate (EVA), ethylene-vinyl alcohol (EVOH), fluoroplastics, PTFE, acrylonitrile-butadiene-styrene (ABS), polyacrylates, polyamides, polyamide-imide, polyimides, polyetherimide, polysulfones,

polyethersulfones, polyketones, polyetheretherketone (PEEK), polycarbonate, polyesters, polycaprolactone, polybutylene terephthalate, polyethylene terephthalate, polylactic acid, polyphenylene oxide, polyphenylene sulfide, thermoplastic polyurethane, polyvinylacetate (PVA), polyvinyl chloride (PVC),
5 polyvinylidene chloride (PVDC), and styrene-acrylonitrile (SAN) copolymer.

18. The method of any one of the above embodiments, wherein the thermoplastic organic polymer is present in about 1 wt.% to about 95 wt.% of the mixture.

19. The method of any one of the above embodiments, wherein the
10 depolymerization catalyst comprises an organic base.

20. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises an inorganic base.

21. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises an organic acid.

15 22. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises an inorganic acid.

23. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises a solid acid selected from at least one of aluminosilicates, acid treated aluminosilicates, zeolites, mixed metal oxides,
20 heteropolyacids, sulfated metal oxides, carbon based solid acids, ion exchange resins, sulfonated polymers, high molecular weight carboxylic acids, and acidic metal salts.

24. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises at least one of a clay, a mixed metal oxide,
25 and a sulfonated metal oxide.

25. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises at least one of kaolin, smectite, illite, chlorites, and palygorskitem sepiolite.

26. The method of any one of the above embodiments, wherein the
30 depolymerization catalyst comprises at least one of montmorillonite, saponite, nontronite (ironsmectite), beidellite, bentonite, and hectorite.

27. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises a clay.

28. The method of any one of the above embodiments, wherein the depolymerization catalyst comprises an acid-washed clay.

29. The method of any one of the above embodiments, wherein the depolymerization catalyst is present in about 0.05 wt.% to about 25 wt.% of the mixture.

30. The method of any one of the above embodiments, wherein the mixture further comprises a filler.

31. The method of any one of the above embodiments, wherein the mixture further comprises at least one of silica, calcium carbonate, and alumina.

32. The method of any one of the above embodiments, wherein the organic polymer comprises about 1 wt.% to about 99 wt.% of the mixture.

33. The method of any one of the above embodiments, wherein the organic polymer comprises about 50 wt.% to about 99 wt.% of the mixture.

34. The method of any one of the above embodiments, wherein both the organic polymer and the silicone are recycled.

35. The method of any one of the above embodiments, wherein the heating is carried out for about 0.1 to about 10 minutes.

36. The method of any one of the above embodiments, wherein the heating is carried out for at least about 30 minutes.

37. The method of any one of the above embodiments, wherein the heating is carried out for at least about 1 hour.

38. The method of any one of the above embodiments, wherein the heating is carried out for up to about 4.5 hours.

39. The method of any one of the above embodiments, wherein the heating is carried out for about 1 to about 4.5 hours.

40. The method of any one of the above embodiments, wherein the heating is carried out such that the temperature of the mixture is below the decomposition temperature of the organic polymer.

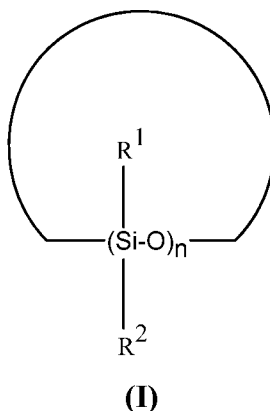
41. The method of any one of the above embodiments, wherein the heating is carried out such that the temperature of the mixture is at least about 5°C below the decomposition temperature of the organic polymer.

42. The method of any one of the above embodiments, wherein the heating is carried out such that the mixture reaches a temperature of at least about 60°C.

43. The method of any one of the above embodiments, wherein the heating is carried out such that the mixture reaches a temperature below about 340°C.

5 44. The method of any one of the above embodiments, wherein the heating is carried out such that the mixture reaches a temperature of about 60°C to about 340°C.

45. The method of any one of the above embodiments, wherein the cyclosiloxane comprises a compound of formula (I):



wherein,

each of $R^1 - R^2$ is at each occurrence independently hydrogen, (C_1-C_{12}) alkyl, (C_6-C_{12}) aryl, (C_6-C_{12}) aryl (C_1-C_{12}) alkyl, or (C_1-C_{12}) alkyl (C_6-C_{12})

15 aryl, optionally substituted with one or more halo; and

n is a whole integer from about 3 to about 20.

46. The method of any one of the above embodiments, wherein the cyclosiloxane comprises one or more cyclic polydimethylsiloxanes, each independently containing about 3 to about 7 silicon atoms.

20 47. The method of any one of the above embodiments, wherein the heating the mixture sufficient to depolymerize at least a portion of the silicone further provides a linear siloxane.

48. The method of any one of the above embodiments, wherein the degassing is carried out by applying a vacuum to the heated mixture.

25 49. The method of any one of the above embodiments, wherein the degassing is carried out by applying to the heated mixture a vacuum of less than about 500 mm Hg.

50. The method of any one of the above embodiments, wherein the degassing is carried out by applying to the heated mixture a vacuum of about 35 mm Hg to about 100 mm Hg.

51. The method of any one of the above embodiments, which is
5 carried out in a continuous mode.

52. The method of any one of the above embodiments, wherein at least one of the contacting, heating, and degassing is carried out in a high shear mechanical device.

53. The method of any one of the above embodiments, wherein at
10 least one of the contacting, heating, and degassing is carried out in an extruder.

54. The method of any one of the above embodiments, wherein at least one of the contacting, heating, and degassing is carried out in a twin-screw extruder, equipped with degassing ports.

55. The method of any one of the above embodiments, wherein the
15 method further comprises forming an extrudate from the residue.

56. The method of any one of the above embodiments, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone located therein.

57. The method of any one of the above embodiments, wherein the
20 method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone located therein, wherein the heating of the extrudate is carried out at a temperature below the decomposition temperature of the organic polymer.

58. The method of any one of the above embodiments, wherein the
25 method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone located therein, wherein the heating of the extrudate is carried out at such that the extrudate reaches a temperature of at least about 120°C.

59. The method of any one of the above embodiments, wherein the
30 method further comprises forming an extrudate from the residue, and heating the extrudate sufficient to depolymerize at least a portion of remaining silicone located therein, wherein the heating of the extrudate is carried out at such that the the extrudate reaches a temperature below about 340°C.

60. The method of any one of the above embodiments, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone
5 located therein, wherein the heating of the extrudate is carried out at such that the extrudate reaches a temperature of about 120°C to about 340°C.

61. The method of any one of the above embodiments, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone
10 located therein, wherein the heating the mixture and the heating the extrudate are each carried out, such that the temperature of the heated mixture is below the temperature of the heated extrudate.

62. The method of any one of the above embodiments, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone
15 located therein, wherein the heating the extrudate is carried out in a pyrolysis kiln or fluidized bed.

63. The method of any one of the above embodiments, wherein neither the mixture nor the heated mixture comprise an organic solvent.

20 64. A method for recycling a silicone waste, the method comprising:

(a) heating a mixture comprising a silicone waste, a thermoplastic organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone waste, to provide a heated mixture comprising cyclosiloxane and a residue;

25 (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane;

(c) forming an extrudate from the residue; and

(d) heating the extrudate, sufficient to depolymerize at least a portion of remaining silicone waste located therein.

30 65. The method of the above embodiment, wherein at least about 75 wt.% of the silicone in the silicone waste is depolymerized.

66. The method of any one of the above embodiments, wherein at least about 90 wt.% of the silicone in the silicone waste is depolymerized.

67. The method of any one of the above embodiments, wherein neither the mixture, the heated mixture, the extrudate, nor the heated extrudate comprise an organic solvent.

68. The method of any one of the above embodiments, wherein the depolymerized material comprises at least one of a cyclic siloxane and an acyclic siloxane monomer.

69. The method of any one of the above embodiments, wherein the depolymerized material comprises one or more cyclic siloxanes and one or more acyclic siloxane monomers.

70. The method of any one of the above embodiments, wherein the depolymerized material obtained therein is subsequently purified.

71. The method of any one of the above embodiments, wherein the depolymerized material obtained therein is subsequently upgraded or converted to a polysiloxane.

72. The method of any one of the above embodiments, wherein the depolymerized material obtained therein is subsequently offered as a commercial product.

73. An article of manufacture obtained from the method of any one of the above embodiments.

20

Examples

Example 1. Extrusion depolymerization of waste PDMS gum

A waste solid PDMS gum, filled with approximately 31 wt.% silica and labeled as RR4875, and Montmorillonite K10, obtained from Sigma Aldrich, were used as the raw materials. The equipment used for this depolymerization step consisted of a 25 mm twin screw extruder on top of which four vacuum ports were installed, and a 1.5 inch diameter single screw extruder connected to the feeding port of the twin screw extruder through a gear pump. The feed rate was calibrated and controlled by the gear pump. The Waste PDMS gum was mixed with 10 wt.% of Montmorillonite K10 and the mixture was fed through the single screw extruder into the twin screw extruder at a rate of 40.57 g/min. The barrel temperature of the twin screw extruder was set at 170 °C, but the actual temperature during the run reached 200 to 210 °C due to the mechanical energy turning into heat. The screw speed was controlled at 300 rpm. A vacuum of 35 to 100 mmHg was maintained. Depolymerization products were collected

as condensed vapor from the four vacuum ports on top of the twin screw extruder barrel. Residual solid was collected at exiting die of the twin screw extruder. The extrudate was continuous and vacuum was maintained well during the run. After 2 hours of steady run, 1095.26 g liquid product was collected, along with 3400 g of residual solid. Based on the solid fed into the twin screw extruder and the solid collected at the exiting die, the conversion was calculated to be approximately 48.8%. Some depolymerization products were apparently not completely collected and lost as vented vapor due to incomplete condensation of the vapor as only 1095.26 g, roughly 75% of theoretical amount was collected. GC-MS identified the products were mainly cyclic siloxanes containing 3 to 7 silicon atoms. The relative amounts of these cyclic siloxanes expressed as weight percentage were determined by GC with a FID detector and were included in Table 1.

Table 1. Composition of products from Example 1.

Ring size*	3	4	5	6	7	Others**
Weight %	6.4	41.4	25.5	13.4	3.1	10.2

*Ring size is expressed as the number of Si atoms in the ring.

**Others are larger rings and small linear siloxanes.

Example 2. Second stage depolymerization of waste PDMS gum

51.1 g of the solid residue collected from the exiting die of the twin screw extruder in Example 1 was placed in a three neck, round bottom flask equipped with a heating mantle, a thermometer, a condenser cooled with water, a receiver under the condenser, and a vacuum pump with accessories. The vacuum was controlled initially at 50 mmHg and then gradually adjusted to 20 mmHg. Temperature was gradually increased and by the time it reached 210 °C liquid product started showing at the bottom of the condenser and was collected. With temperature maintained, liquid collection lasted for an hour. The temperature was increased to 245 °C and maintained for 5 hours, but no additional liquid was collected. Once the flask is cooled, it was found that 15.3 g of liquid was collected as product, and the solid lost 18.4 g of weight, corresponding to a calculated additional conversion of 40.11% from this step, and a total conversion

from both steps, first in example 1 and second in example 2, of 88.19%.

Compositions of the products were similar to those obtained in Example 1.

Example 3. Extrusion depolymerization of mixture of waste PDMS gum and waste cured silicone tubing

The same equipment as in Example 1 was used except that the gear pump in between the single screw extruder and the twin screw extruder was removed to facilitate flow of mixture with solid cut tubing pellets. A sample of waste silicone medical tubing was obtained and cut into pieces approximately 7 mm by 7 mm in size. A low density polyethylene sample was purchased from Sigma Aldrich with a melt index of 55 g/10 min measured according to ASTM D 1238 at 190 °C/2.16 kg. A mixture of 7 kg tubing, 5.6 kg waste solid PDMS gum as used in Example 1, 1.26 kg Montmorillonite K10, and 1.575 kg polyethylene was made. The feeding rate of the single screw extruder with this mixture was calibrated as a function of screw rotating speed. And the feeding rate was controlled at 14 g/min. The twin screw extruder screw speed was set at 300 rpm and the barrel temperature was set at 160 °C. As in Example 1, depolymerization products were collected as condensed vapor from the four vacuum ports, and residual solids were collected at the exiting die of the twin screw extruder. After 2 hours of steady run, 328.91 g of liquid product was collected along with 1325 g of residual solid. The conversion achieved in this step was 41.53%, and approximately 94% of depolymerization products were collected, a more efficient collection than in Example 1. The composition of the products was identified by GC-MS and the relative amount of each component was determined by GC-FID. Results were included in Table 3.

Table 2 Compositions of products from Example 3.

Ring size*	3	4	5	6	7	Others**
Weight %	7	42.3	26.9	12.3	2.4	9.1

*Ring size is expressed as the number of Si atoms in the ring.

**Others are larger rings and small linear siloxanes of various length.

Example 4. Second stage depolymerization of mixture of waste PDMS gum and waste cured silicone tubing

50 g of the solid residue collected from the exiting die of the twin screw extruder in Example 3 was placed in a three neck, round bottom flask equipped as described in Example 2. A similar heating/vacuum/vapor

5 condensation/collection process was carried out. The final temperature was increased to 260 °C and maintained for 6 hours until no additional liquid was collected. Once the flask is cooled, it was found that 12.9 g of liquid was collected as product, and the solid lost 15.8 g of weight, corresponding to a calculated additional conversion of 25.32% from this step, and a total conversion
10 from both steps, first in example 3 and second in example 4, of 66.85%. Approximately 81.6% of the depolymerization product was collected as liquid in Example 4. The composition of the collected products was dominated by cyclic siloxanes but also contained a small amount of T_nD_m siloxanes.

Table 3. Compositions of products from Example 4.

Ring size	3	4	5	6	7	Others**
Weight %	58.5	15.3	3.9	2.1	1.3	18.9

15 **Others contain larger rings and T_nD_m siloxanes.

Example 5. Depolymerization, experiments 1-14

Starting materials: RR4875 Silicone Gum Waste, Low Density Polyethylene (MI 25 g/10 min.) from Sigma Aldrich, and Montmorillonite K10
20 from Sigma Aldrich.

Equipment: 25 mm Twin Screw Extruder.

Feeder: Bonnot 2.5" diameter single screw extruder.

Exp t.	Bonno t Setting , rpm	Feed Rate, g/min	Expt. Length , h	Liquid collecte d, g	Solid Collecte d, g	Higher Bound of conversion		Process Stability	Material Type	TSE rpm	TSE torqu e	Set TSE Temp , °C
						Higher Bound of conversion	Lower Bound of conversion					
1	3.27	40	1	413.25	1700	54.95	36.84	Good	RR4875 + 10% MM K10 + 20% Polyethylene	600	32%	170
2	3.27	40	1	427	1800	47.10	36.12	Good	RR4875 + 10% MM K10 + 20% Polyethylene	600	32%	210
3	2.45	30	1	341.73	1230	59.66	40.96	Good	RR4875 + 10% MM K10 + 20% Polyethylene	600	32%	170
4	1.65	20	1	323	775	66.73	55.42	Good	RR4875 + 10% MM K10 + 20% Polyethylene	600	32%	170
5	1	11.326	2	413.4	875	67.11	60.45	Good	RR4875 + 10% MM K10	600	32%	170

[illegible]

11	1	unkown	1	16.59	84.4	Combined lower bound of two step conversion = 74.38%	54.71	Good	Extrudate from expt. 9	300	See below *
12	3.35	40.57	2	1095.26	3400	48.08	38.84	Good	RR4875 + 10% MM K10	300	170
13	1	11.326	1	See comment 1 below**				Poor**	RR4875 + 10% MM K10	300	170

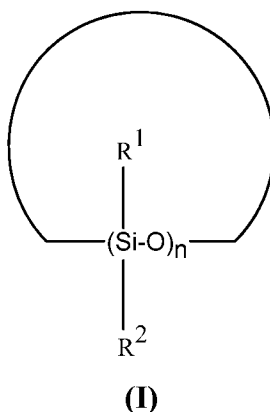
*This one had a more complicated temperature setting for the multiple zones of the twin screw extruder: Zone 1: 15; Zones 2-5: 150; Zones 6+7: 160; Zones 8+9: 180; Zones 10+11: 200; Zone 12: 190; and Zone 13: 25 °C. ** The process was very unstable. The first 12 minutes, vapor was visibly coming out from the vacuum ports, and the extruded mass was dry and hard, indicating complete depolymerization and removal of cyclics. From 12 to 20 minutes, no vapor was seen coming out from the last two ports. The extruded mass became softer, soft in touch even after cooling. After 20 minutes, no vapor was seen coming out of any of the vacuum ports. The extruded mass was basically the same as the fed gum, no sign of decomposition was seen. After the run, vacuum ports were all disassembled and examined. They were all completely clogged by dry powder and dark material. This was in contrast to the previous 12 runs with polyethylene. These runs were successful and stable without ports clogged.

CLAIMS

We claim:

1. A method comprising:
 - (a) heating a mixture comprising a silicone, an organic polymer, and a depolymerization catalyst, wherein the heating is sufficient to depolymerize at least a portion of the silicone, to provide a heated mixture comprising cyclosiloxane and a residue; and
 - (b) degassing the heated mixture to remove at least a portion of the cyclosiloxane.
2. The method of any one of the above claims, wherein the silicone comprises an organopolysiloxane.
3. The method of any one of the above claims, wherein the silicone is present in about 50 wt.% to about 99 wt.% of the mixture.
4. The method of any one of the above claims, wherein the organic polymer is a thermoplastic organic polymer comprising at least one of low density polyethylene (LDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE).
5. The method of any one of the above claims, wherein the organic polymer is a thermoplastic organic polymer, present in about 50 wt.% to about 95 wt.% of the mixture.
6. The method of any one of the above claims, wherein the depolymerization catalyst is present in about 0.05 wt.% to about 25 wt.% of the mixture.
7. The method of any one of the above claims, wherein the mixture further comprises at least one of silica, calcium carbonate, and alumina.

8. The method of any one of the above claims, wherein the heating is carried out for about 1 to about 4.5 hours.
9. The method of any one of the above claims, wherein the heating is carried out such that the mixture reaches a temperature of about 60°C to about 340°C.
10. The method of any one of the above claims, wherein the cyclosiloxane comprises a compound of formula (I):



wherein,

each of R^1 - R^2 is at each occurrence independently hydrogen, (C_1-C_{12}) alkyl, (C_6-C_{12}) aryl, (C_6-C_{12}) aryl (C_1-C_{12}) alkyl, or (C_1-C_{12}) alkyl (C_6-C_{12}) aryl, optionally substituted with one or more halo; and
 n is a whole integer from about 3 to about 20.

11. The method of any one of the above claims, wherein the degassing comprises applying to the heated mixture a vacuum of about 35 mm Hg to about 100 mm Hg.
12. The method of any one of the above claims, wherein at least one of the contacting, heating, and degassing is carried out in a twin-screw extruder, equipped with degassing ports.
13. The method of any one of the above claims, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate

sufficiently to depolymerize at least a portion of remaining silicone located therein.

14. The method of any one of the above claims, wherein the method further comprises forming an extrudate from the residue, and heating the extrudate sufficiently to depolymerize at least a portion of remaining silicone located therein, wherein the heating of the extrudate is carried out at such that the extrudate reaches a temperature of about 120°C to about 340°C.

15. The method of any one of the above claims, wherein neither the mixture nor the heated mixture comprise an organic solvent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/018028

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J11/16 C08J11/18
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)
C08J

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

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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

3 June 2014

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/018028

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