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(54) Title: POLYMERIC MATERIAL FOR ACCOMMODATING INTRAOCULAR LENSES

(57) Abstract: The disclosure relates generally to a polymeric material for use in accommodating intraocular lenses for implantation in a lens chamber of a subject's eye. The present disclosure is directed to a polymeric material which comprises a fluorosilicone polymer and a silica component. The presently disclosed polymeric material is both optically clear and has a sufficiently low Young's modulus such that it can effectively respond to the eye's natural accommodative forces and thus can be used in accommodating intraocular lenses. When used in the fabrication of an intraocular lenses, the polymeric material disclosed herein protect the physical characteristics of the lens as the added hydrophobicity of the fluorosilicone polymer allows it to effectively resist diffusion of fluid from the eye and the adhesion of biologica materials.

POLYMERIC MATERIAL FOR ACCOMMODATING INTRAOCULAR LENSES

FIELD

The disclosure relates generally to a polymeric material for use in accommodating intraocular lenses for implantation in a lens chamber of a subject's eye.

BACKGROUND

Surgical procedures on the eye have been on the rise as technological advances permit for sophisticated interventions to address a wide variety of ophthalmic conditions. Patient acceptance has increased over the last twenty years as such procedures have proven to be generally safe and to produce results that significantly improve patient quality of life.

Cataract surgery remains one of the most common surgical procedures, with over 16 million cataract procedures being performed worldwide. It is expected that this number will continue to increase as average life expectancies continue to rise. Cataracts are typically treated by removing the crystalline lens from the eye and implanting an intraocular lens ("IOL") in its place. As conventional IOL devices are primarily focused for distance visions, they fail to correct for presbyopia and reading glasses are still required. Thus, while patients who undergo a standard IOL implantation no longer experience clouding from cataracts, they are unable to accommodate, or change focus from near to far, from far to near, and to distances in between.

Surgeries to correct refractive errors of the eye have also become extremely common, of which LASIK enjoys substantial popularity with over 700,000 procedures being performed per year. Given the high prevalence of refractive errors and the relative safety and effectiveness of this procedure, more and more people are expected to turn to LASIK or other surgical procedures over conventional eyeglasses or contact lenses. Despite the success of LASIK in treating myopia, there remains an unmet need for an effective surgical intervention to correct for presbyopia, which cannot be treated by conventional LASIK procedures.

As nearly every cataract patient also suffers from presbyopia, there is convergence of market demands for the treatment of both these conditions. While there is a general acceptance among physicians and patients of having implantable intraocular lens in the treatment of cataracts, similar procedures to correct for presbyopia represent only 5% of the U.S. cataract market. There is therefore a need to address both ophthalmic cataracts and/or presbyopia in the growing aging population.

SUMMARY

The present disclosure is directed to a polymeric material which comprises a fluorosilicone polymer and a silica component. The presently disclosed polymeric material is both optically clear and has a sufficiently low Young's modulus such that it can effectively respond to the eye's natural accommodative forces and thus can be used in accommodating intraocular lenses. When used in the fabrication of an intraocular lenses, the polymeric material disclosed herein protect the physical characteristics of the lens as the added hydrophobicity of the fluorosilicone polymer allows it to effectively resist diffusion of fluid from the eye and the adhesion of biological materials.

Accordingly, in one aspect, provided herein is a polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g.

In another aspect, provided herein is an implantable intraocular lens (IOL) comprising a polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g.

In still another aspect, provided herein is an intraocular lens (IOL) device comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g. In one aspect, the intraocular lens (IOL) device comprises

(a) a first lens comprised of a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g having a first Young's modulus;

(b) a second lens in spaced relation to the first lens along a central optical axis; and

(c) a circumferential portion encircling the first and second lens, the circumferential portion comprising an outer peripheral edge;

wherein at least one of a portion of the second lens and a portion of the circumferential portion is made of a material having a second Young's modulus; and wherein the first Young's modulus is less than the second Young's modulus.

Other objects, features and advantages of the described embodiments will become apparent to those skilled in the art from the following detailed description. It is to be understood, however, that the detailed description and specific examples, while indicating various embodiments of the present invention, are given by way of illustration and not imitation. Many changes and modifications within the scope of the present invention may be made without departing from the spirit thereof, and the invention includes all such modifications.

DETAILED DESCRIPTION

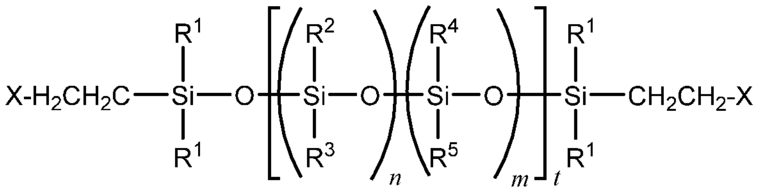
Specific, non-limiting embodiments of the present invention will now be described with reference to the drawings. It should be understood that such embodiments are by way of example and are merely illustrative of but a small number of embodiments within the scope of the present invention. Various changes and modifications obvious to one skilled in the art to which the present invention pertains are deemed to be within the spirit, scope and contemplation of the present invention as further defined in the appended claims.

Polymeric Material

The present disclosure is directed to a polymeric material comprising a fluorosilicone polymer and a silica component which is both optically clear and has a sufficiently low modulus such that it can effectively respond to the eye's natural accommodative forces and thus be used in accommodating intraocular lenses.

In one embodiment, the presently disclosed polymeric material comprises a fluorosilicone polymer and up to about 30 weight% of a silica component. The fluorosilicone polymer described herein is a crosslinked copolymer of dialkyl, diphenyl or phenylalkyl siloxane and a fluorinated dialkyl siloxane. Typically, the fluorosilicone polymer is a crosslinked copolymer of dialkyl, diphenyl or phenylalkyl siloxane and trifluoroalkyl(alkyl)siloxane, but can be a terpolymer or higher order polymer of diphenyl and/or phenylalkyl siloxane, dialkyl siloxane and trifluoroalkyl(alkyl)siloxane. In certain embodiments, the fluorosilicone polymer is a crosslinked copolymer of dialkyl siloxane, such as dimethyl siloxane, and trifluoroalkyl(alkyl)siloxane, such as 3,3,3-trifluoropropylmethyl siloxane. The ratio of dialkyl siloxane and trifluoroalkyl(alkyl)siloxane can be adjusted to tune the physical properties of the fluorosilicone polymer. For example, increasing the trifluoroalkyl(alkyl)siloxane can increase the hydrophobicity of the resulting fluorosilicone polymer. In some embodiments, the fluorosilicone polymer typically comprises at least about 25 mole% trifluoroalkyl(alkyl)siloxane, or about 25 mole% trifluoroalkyl(alkyl)siloxane, or about 30 mole% trifluoroalkyl(alkyl)siloxane, or about 35 mole% trifluoroalkyl(alkyl)siloxane, or about 40 mole% trifluoroalkyl(alkyl)siloxane, or about 50 mole% trifluoroalkyl(alkyl)siloxane or from about 25 mole% to about 50 mole%, or from about 25 mole% to about 40 mole% trifluoroalkyl(alkyl)siloxane.

In one embodiment, the fluorosilicone polymer is represented by formula (I):



$$X\text{-}H_2CH_2C-\overset{R^1}{\underset{R^1}{Si}}-O-\left[\left(\overset{R^2}{\underset{R^3}{Si}}-O\right)_n\left(\overset{R^4}{\underset{R^5}{Si}}-O\right)_m\right]_t-\overset{R^1}{\underset{R^1}{Si}}-CH_2CH_2\text{-}X$$

(I)

wherein:

n and m are each independently 0 to about 500;

t is about 100 to about 1000;

each R^1 is independently alkyl or aryl;

R^2 is haloalkyl;

R^3 is alkyl or haloalkyl;

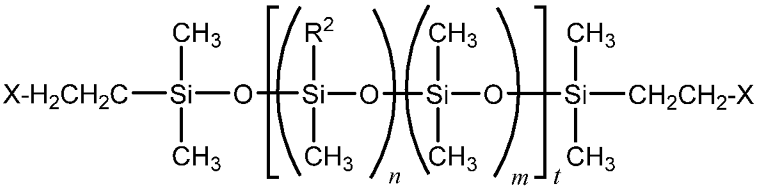
R^4 and R^5 are independently alkyl, haloalkyl or aryl; and

each X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I).

In one embodiment, n is about 50, or about 100, or about 125, or about 150, or about 200, or about 250, or about 300, or about 350, or about 400, or about 450, or about 500. In one embodiment, m is about 50, or about 100, or about 125, or about 150, or about 200, or about 250, or about 300, or about 350, or about 400, or about 450, or about 500. In another embodiment, *n* is about 100, and *m* is about 150.

In any embodiment, *t* is about 100, or about 125, or about 150, or about 200, or about 250, or about 300, or about 350, or about 400, or about 450, or about 500, or about 550, or about 600, or about 650, or about 700, or about 750, or about 800, or about 850, or about 900, or about 950, or about 1000.

In one embodiment, each R^1 is alkyl. Suitable alkyl groups include, but are not limited to, C_1-C_6 alkyl groups such as methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, n-pentyl, n-hexyl, and the like. In another embodiment, each R^1 is methyl. In one embodiment, R^3 is alkyl, such as defined for R^1. In another embodiment, R^3 is methyl. In one embodiment, R^4 is alkyl, such as defined for R^1. In another embodiment, R^4 is methyl. In one embodiment, R^5 is alkyl, such as defined for R^1. In another embodiment, R^5 is methyl. In yet another embodiment, R^4 and R^5 are methyl. In still another embodiment, the fluorosilicone polymer is represented by formula (IA):



$$\mathrm{X{-}H_2CH_2C}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}-\left[\left(\underset{CH_3}{\overset{R^2}{\mathrm{Si}}}-\mathrm{O}\right)_n\left(\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right)_m\right]_t-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{CH_2CH_2{-}X}$$

(IA)

wherein:

n is from 1 to about 500;

m is from 0 to about 500;

t is about 100 to about 1000;

R^2 is haloalkyl;

R^3 is alkyl or haloalkyl; and

each X is a crosslinker which links the polymer of formula (IA) with a second polymer of formula (IA).

In one embodiment, R^2 is a haloalkyl group comprising from 1 to 3 halo (provided at least one is fluoro) substituents. Exemplary haloalkyl groups include, but are not limited to, fluoromethyl, 2-fluorethyl, 2,2-difluoroethyl, and 3,3,3-trifluoropropyl. In one embodiment, R^2 is 3,3,3-trifluoropropyl.

The crosslinker is typically a methylhydrosiloxane-dimethylsiloxane copolymer with a methyl-hydrogen content of from about 30 to about 70 mole%. In some embodiments, the crosslinker has a chain length of from about 5 to about 30 repeating Si units (i.e., degree of polymerization).

In certain embodiments, the polymeric material provided herein has a degree of polymerization of from about 200 to about 500, or from about 300 to about 500, or about 400, or about 450.

In order to be used as an intraocular lens material, the polymeric material described herein should be optically clear. However, the fluorosilicone polymer and the silica component are not index matched. Thus the optical properties of the polymeric material must be maintained as the modulus is increased. Advantageously, the optical properties of the presently disclosed polymeric material can be tuned independently from the modulus. Several different factors contribute to the optical properties of the polymeric material, including the amount and particle size of the silica component.

Since the refractive index of the fluorosilicone polymer is low, it is contemplated that the particle size of the silica component should be as small as possible in order to obtain superior optical characteristics. In certain embodiments, the polymeric material provided herein has a refractive index of from about 1.35 to about 1.40, or from about 1.37 to from about 1.39, or about 1.38. Accordingly, the silica component as used herein has a surface area of at least about 280 m^2/g, or at least about 300 m^2/g, or at least about 310 m^2/g, or at least about 320 m^2/g, or at least about 330 m^2/g, or at least about 340 m^2/g, or at least about 350 m^2/g. In certain embodiments, the silica component has an average particle size of less than about 11 nanometers. Fumed silica having an average particle size of about 7 nanometers in diameter is particularly suitable because the small particle size does not interfere with the wavelength of visible light and contributes to an improved optical resolution in the cured composition. Commercial fumed silica with particle sizes as low as 7 nm are commercially available (e.g., CABOT and Sigma).

Typically, the silica component is present in an amount up to about 30 weight%, or 27 weight%, or about 25 weight%, or about 23 weight%, or about 20 weight%, or from about 20 to about 30 weight%.

The silica component as used herein is fumed or "activated" silica, which has been treated with a silazane. The amount of silica component should be such that the polymeric material is sufficiently reinforced, yet remains optically clear. Suitable silazanes and methods for carrying out the fumed silica treatment include the *in situ* reaction of small particle size fumed silica and are well known in the art. In such reactions, the silazane (e.g., hexamethyldisilazane) readily reacts with the hydroxyl functionalities on fumed silica, forming a trimethylsiloxane coating on the silica surface. In certain embodiments, the polymeric material provided herein has a Young's modulus of from about 10 psi to about 150 psi, or from about 50 psi to about 100 psi, or about 70 psi.

Other physical characteristics of the polymeric material can be modulated as well. In certain embodiments, the polymeric material provided herein has a tensile strength of from about 500 psi to about 1200 psi, or from about 700 psi to about 1000 psi, or about 900 psi. In certain embodiments, the polymeric material provided herein has a percent elongation of from about 400% to about 1000%, or about 600%.

Also provided herein are methods for making the above-described polymeric material. In certain embodiments, the method comprises the steps of:

(a) combining a vinyl end-capped fluorosilicone polymer with up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g, to obtain a fluorosilicone base composition;

(b) adding a crosslinking agent and a curing agent to the fluorosilicone base composition; and

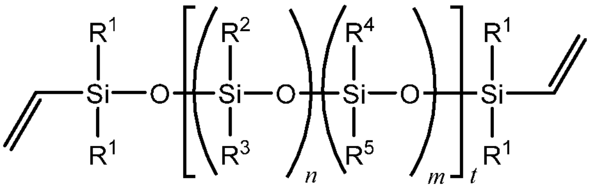
(c) curing the fluorosilicone base composition to obtain the polymeric material.

The vinyl end-capped fluorosilicone polymer can be synthesized using known methods from commercially available starting materials or purchased from commercial sources. For example, a vinyl end-capped trifluoropropylmethylsiloxane – dimethylsiloxane copolymer having a molecular weight of about 25,000 to about 35,000 – is commercially available from

Gelest. Alternatively, the vinyl end-capped fluorosilicone polymercan be synthesized as described in Example 1, for example. Suitable starting materials include, but are not limited to, alkylsiloxanes (e.g., octamethylcyclotetrasiloxane), haloalkylsiloxanes (e.g., trifluoropropyltrimethylcyclosiloxane), and the like. Suitable vinyl endblockers include, but are not limited to, vinyl-endblocked dimethyl siloxane oligomer.

In one embodiment, the fluorosilicone polymer has a long chain length, having a molecular weight of greater than 35,000 daltons, or greater than 50,000 daltons and, or greater than 70,000 daltons are desired.

In one embodiment, the fluorosilicone polymeris a compound of formula (II):



(II)

wherein:

n and m are each independently 0 to about 500;

t is from about 100 to about 1000;

each R^1 is independently alkyl or aryl;

R^2 is haloalkyl;

R^3 is alkyl or haloalkyl; and

R^4 and R^5 are independently alkyl, haloalkyl or aryl.

The polymeric material described herein has a degree of crosslinking such that the material has a sufficiently low modulus to minimize any potential deformation caused by forces applied during its use as, for example, an accommodating intraocular lens, yet also be sufficiently solid as to minimize the permeation of the gel. In certain embodiments, the polymeric material is lightly crosslinked, having less than about 5 parts per hundred (pph) crosslinker, or less than about 4 pph, or less than about 2 pph, or less than about 1 pp, or about 1 pph. The crosslinker is typically a methylhydrosiloxane-dimethylsiloxane copolymer with a methyl-hydrogen content of from about 30 to about 70 mole%. In some embodiments, the crosslinker has a chain length of from about 5 to about 30 repeating Si units (i.e., degree of polymerization).

In one embodiment, the curing step comprises adding a platinum catalyst. The platinum group metal catalyst can be any of the compatible platinum group metal-containing catalysts known to catalyze the addition of silicone-hydrogen atoms to silicon-bonded vinyl radicals. Platinum group metal-containing catalysts can be any of the known forms which are compatible, such as platinic chloride, salts of platinum, chloroplatinic acid and various complexes, for example, silicone complexes with platinum metal-containing groups. The platinum group metal-containing catalyst can be used in any catalytic quantity, such as in an amount sufficient to provide at least about 0.1 ppm weight of platinum group metal (as elemental metal) based on the total weight of the composition. In certain embodiments, at least about 10 ppm, or at least about 20 ppm, or at least 30 ppm, or at least about 40 ppm by weight of platinum catalyst was used.

Implantable Intraocular Lens (IOL)

A device implanted in the eye naturally becomes exposed to the fluid in the eye and the fluid can, over time, diffuse through the device and have unintended and/or undesired effects on the physical characteristics of the device. Attempts have been made to coat ophthalmic devices with barrier layers to prevent such diffusion, but these procedures can be costly and time consuming. In addition, if an ophthalmic device contains a chamber or channel within the device which contains a fluid, there is a risk that that fluid can diffuse out of its fluid chamber and into the polymeric material. This results in a decrease in the amount of fluid that can be utilized by the IOL, as well as to possibly alter the physical characteristics of the polymeric material. Fluorocarbon-containing silicone monomers can enhance a polymer's resistance to the diffusion of fluid, and as such, the polymeric material described herein can be used in ophthalmic devices to resist the diffusion of fluid into or out of the device.

The IOLs can be fabricated from the disclosed polymeric material using known molding techniques, such as disposable or polished stainless steel mold, having a mold cavity in the shape required for the correct refraction of light for the material. In practice, the uncured fluorosilicone base composition is introduced into the mold cavity, in an amount dictated by considerations relating to the lens size, refractive power, and structure, and then cured. Several methods of molding the lens can be employed, including injection molding, liquid injection molding, compression molding, and transfer molding.

Intraocular Lens (IOL) Device

The presently disclosed intraocular lenses can be used in an intraocular device for implantation in a patent. Such devices are known in the art, and include, for example, those described in US 7,662,180 and US 7,875,661.

In certain embodiments, the presently disclosed intraocular lenses can be used as a power changing lens in a two-part accommodating IOL device in which the power changing lens and a primary lens are in sliding contact with one another within a lens chamber. In such systems, the power changing lens is sized and shaped to take on and respond to the radially-inward forces which are applied along the peripheral edge of the lens. In contrast, the primary lens does not participate in providing an accommodative response and thus is sized and shaped so as to avoid interfering or resisting the radial compressive forces that are applied to the power changing lens. This may be accomplished by controlling the relative diameters and thicknesses of the power changing lens and the primary lens to maximize the extent to which the radial compressive forces are applied onto the power changing lens and to minimize the extent to which these forces are applied onto the primary lens.

Accordingly, in one embodiment, provided herein is an intraocular lens (IOL) device comprising:

(a) a first lens comprised of the polymeric material as described herein having a first Young’s modulus;

(b) a second lens in spaced relation to the first lens along a central optical axis; and

(c) a circumferential portion encircling the first and second lens, the circumferential portion comprising an outer peripheral edge;

wherein at least one of a portion of the second lens and a portion of the circumferential portion is made of a material having a second Young’s modulus; and wherein the first Young’s modulus is less than the second Young’s modulus.

In practice, the first lens (i.e., the power changing lens) and the second lens (i.e., the primary lens) are in sliding contact with one another within a lens chamber. The lens chamber is filled with a fluid or gel having specific physical and chemical characteristics to enhance the range of refractive power provided by the IOL during accommodation. The fluid or gel is selected such that it cooperates with the power changing lens in providing a sufficient range of accommodation of up to at least 3 diopters, preferably up to at least 5 diopters, preferably up to at least 10 diopters and most preferably up to at least 15 diopters.

In addition, a lens comprised of the polymeric material described herein has a reduced likelihood of buckling in a patient from contact with the primary lens as the surface is significantly more oleophobic than other polymers typically used for IOLs.

In addition to use in an IOL, the polymeric material of the present disclosure can also be used in other ophthalmic devices such as, but not limited to, contact lenses, keratoprostheses, capsular bag extension rings, corneal inlays, corneal rings, or other ophthalmic devices. An exemplary alternative use would be in the field of breast implants, such that the polymers can be used as an exterior shell-like material to prevent leakage of an internal material.

EXAMPLES

Example 1

An exemplary polymeric material according to the present disclosure was prepared as follows.

Vinyl endblocked 40 mole% fluorosilicone polymer

A vinyl endblocked 40 mole% fluorosilicone polymer for use in the fluorosilicone base was prepared as follows. 140 parts octamethylcyclotetrasiloxane (D4 cyclics), 100 parts trifluoropropyltrimethylcyclosiloxane (D3 fluorocyclics), 3.2 parts vinyl-endblocked dimethyl siloxane oligomer (vinyl endblocker), and 0.1 parts potassium siloxanolate catalyst were agitated in a polymerization vessel and heated to about 150 °C. At 150 °C, potassium siloxanolate catalyst was added to the polymerization vessel. Once polymerization was visually observed by an increased viscosity, polymerization was continued for about 3 hours.

After about 3 hours, the catalyst was de-activated by purging polymer with CO_2 for 1 hour and the polymer exposed to reduced pressure (minimum of 27” Hg vacuum) at a temperature of from about 150 °C to about 180 °C until the volatile content reached an amount below about 3%.

Fluorosilicone Base

100 parts of the vinyl endblocked 40 mole% fluorosilicone polymer, 9 parts hexamethyldisilizane (HMDZ) and 3 parts water were added to a mixing vessel (e.g., sigma blade mixer). Once mixed, 60 parts activated silica (Tokuyama QS-30C fumed silica) was added in multiple additions until the silica was fully mixed into the fluorosilicone polymer. The composition was mixed at 80 °C for about 30 minutes, at which time the mixing vessel was heated to about 150 °C for about 3 hours under vacuum.

After about 3 hours, the heat and vacuum were removed. While the fluorosilicone base was still hot, additional fluorosilicone polymer was slowly added to the polymerization vessel until the silica content was reduced to approximately 25 parts. The fluorosilicone base was then dispersed in chlorinated solvent (i.e., perchloroethylene) to approximately 30% solids content, filtered through 1 micron media filter and subjected to heat and vacuum to remove solvent.

Polymeric material comprising a fluorosilicone polymer

Equal parts of A and B (Table 1) were mixed together, vacuum de-aired, and press cured in an ASTM test slab mold for about 10 minutes at 302 °F. Cured test slab was allowed to equilibrate at room temperature for a minimum of 3 hours.

Table 1

Part A	**Part B**
100 part fluorosilicone base	100 parts fluorosilicone base
5-15 ppm platinum catalyst	2 parts methyl hydrogen siloxane crosslinker
	0.3 pph methyl vinyl cyclosilicone inhibitor

Mechanical properties of the fluorosilicone polymer are shown in Table 2. Surprisingly, the fluorosilicone polymer as described herein exhibits an enhanced tensile strength while maintaining a low modulus when compared to a non-fluorinated silicone polymer. In addition, it is contemplated that the fluorosilicone polymer described herein maintains a suitable optical clarity due to the low silica content.

	Fluorosilicone polymer	Non-fluorinated silicone polymer

Durometer (Shore A)	20	20
Tensile strength	900 psi	475 psi
% elongation	600%	300%
100% modulus	70 psi	65 psi

The invention described and claimed herein is not to be limited in scope by the specific preferred embodiments disclosed herein, as these embodiments are intended as illustrations of several aspects of the invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

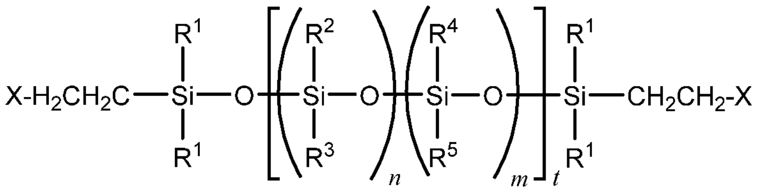
CLAIMS

1. A polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g.

2. The polymeric material of claim 1, wherein the silica component has a surface area of from about 280 m^2/gram to about 350 m^2/g.

3. The polymeric material of claim 1, comprising about 27%, or about 25%, or about 23%, or about 20% of the silica component.

4. The polymeric material of claim 1, wherein the fluorosilicone polymer comprises a polymer of formula (I):



$$X\text{-}H_2CH_2C-\overset{R^1}{\underset{R^1}{Si}}-O-\left[\left(\overset{R^2}{\underset{R^3}{Si}}-O\right)_n\left(\overset{R^4}{\underset{R^5}{Si}}-O\right)_m\right]_t-\overset{R^1}{\underset{R^1}{Si}}-CH_2CH_2\text{-}X$$

(I)

wherein:

n and m are each independently 0 to about 500;

t is about 100 to about 1000;

each R^1 is independently alkyl or aryl;

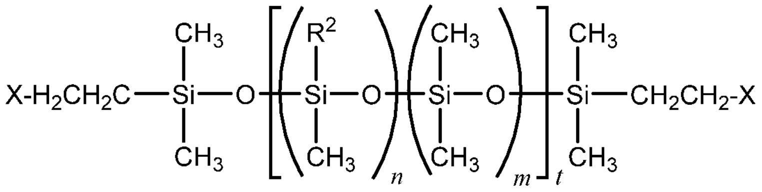
R^2 is haloalkyl;

R^3 is alkyl or haloalkyl;

R^4 and R^5 are independently alkyl, haloalkyl or aryl; and

each X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I).

5. The polymeric material of claim 3, wherein the fluorosilicone polymer of formula (I) is represented by formula (IA):



$$X\text{-}H_2CH_2C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\left(\overset{R^2}{\underset{CH_3}{Si}}-O\right)_n\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_m\right]_t-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2CH_2\text{-}X$$

(IA)

wherein:

n is from 1 to about 500;

m is from 0 to about 500;

t is about 100 to about 1000;

R^2 is haloalkyl;

R^3 is alkyl or haloalkyl; and

each X is a crosslinker which links the polymer of formula (IA) with a second polymer of formula (IA).

6. The polymeric material of claim 4, wherein R^2 is 3,3,3-trifluoropropyl.

7. The polymeric material of claim 6, comprising at least about 25 mole% trifluoropropyl content.

8. The polymeric material of claim 1, having a refractive index of from about 1.35 to about 1.40, or from about 1.37 to from about 1.39, or about 1.38.

9. The polymeric material of claim 1, having a tensile strength of from about 500 psi to about 1200 psi, or from about 700 psi to about 1000 psi, or about 900 psi.

10. The polymeric material of claim 1, having a percent elongation of from about 400% to about 1000%, or about 600%.

11. The polymeric material of claim 1, having a degree of polymerization of from about 200 to about 500, or about 400.

12. The polymeric material of claim 1, having a Young's modulus of from about 10 psi to about 150 psi, or from about 50 psi to about 100 psi, or about 70 psi.

13. A polymeric material comprising a crosslinked dialkyl siloxane-trifluoroalkyl(alkyl)siloxane copolymer, and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g.

14. A polymeric material comprising a crosslinked dimethyl siloxane-3,3,3-trifluoropropylmethyl siloxane copolymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g.

15. The polymeric material of any one of claims 1-14, wherein the crosslinker is a methylhydrosiloxane-dimethylsiloxane copolymer.

16. The polymeric material of claim 15, wherein the crosslinker has a chain length of from about 5 to about 30 repeating Si units.

17. The polymeric material of claim 15, wherein the crosslinker has a methyl-hydrogen content of from about 30 to about 70 mole%.

18. An implantable intraocular lens (IOL) comprising the polymeric material of any one of the preceding claims.

19. A method of making the polymeric material of claim 1, comprising the steps of:

(a) combining a vinyl end-capped fluorosilicone polymer with up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m^2/g, to obtain a fluorosilicone base composition;

(b) adding a crosslinking agent and a curing agent to the fluorosilicone base composition; and

(c) curing the fluorosilicone base composition to obtain the polymeric material.

20. The method of claim 19, wherein step b) comprises:

adding the crosslinking agent to a first portion of the fluorosilicone base composition of step a), and adding the curing agent to a second portion of the fluorosilicone base composition of step a), and

mixing the first and second portions prior to step c).

21. The method of claim 19 or 20, wherein the first portion of the fluorosilicone base composition further comprises an inhibitor.

22. The method of any one of claims 19-21, wherein the curing agent is a platinum catalyst.

23. The method of any one of claims 19-22, wherein the silica component has a surface area of from about 280 m^2/g to about 350 m^2/g.

24. The method of any one of claims 19-23, wherein the silica component is provided by contacting silica with hexamethyldisilizane and water.

25. An intraocular lens (IOL) device comprising a lens comprised of the polymeric material of any one of claims 1-17.

26. An intraocular lens (IOL) device comprising:

(a) a first lens comprised of the polymeric material of any one of claims 1-17 having a first Young's modulus;

(b) a second lens in spaced relation to the first lens along a central optical axis; and

(c) a circumferential portion encircling the first and second lens, the circumferential portion comprising an outer peripheral edge;

wherein at least one of a portion of the second lens and a portion of the circumferential portion is made of a material having a second Young's modulus; and

wherein the first Young's modulus is less than the second Young's modulus.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/051512

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A61K 31/695 (2016.01)
CPC - C08G 77/70 (2015.12)
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)
IPC(8) - A61F 2/16; A61K 31/695 (2016.01)
CPC - A61F 2/16; A61K 31/695; C08G 77/70; C08L 83/06 (2015.12)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 623/6.11, 6.56; IPC(8) - A61F 2/16; A61K 31/695 (2016.01); CPC - A61F 2/16; A61K 31/695; C08G 77/70; C08L 83/06 (2015.12) (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, SureChEMBL, PubChem, Google Scholar.
Search terms used: 1,3-diethyltetramethyldisiloxane, 1,3-diethyl-1,1,3,3-tetramethyl-disiloxane, 1,3-divinyltetramethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane, methylhydrosiloxane-dimethylsiloxane, crosslink+, cross link+, silica, silicon dioxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/0069178 A1 (RASTOGI et al) 30 March 2006 (30.03.2006) entire document	1-4, 8-17
A	US 2006/0135477 A1 (HAITJEMA et al) 22 June 2006 (22.06.2006) entire document	1-4, 8-17
A	US 8,257,827 B1 (SHI et al) 04 September 2012 (04.09.2012) entire document	1-4, 8-17
A	US 5,854,310 A (MAXSON) 29 December 1998 (29.12.1998) entire document	1-4, 8-17
A	US 5,583,178 A (OXMAN et al) 10 December 1996 (10.12.1996) entire document	1-4, 8-17
A	US 5,171,773 A (CHAFFEE et al) 15 December 1992 (15.12.1992) entire document	1-4, 8-17
A	PUBCHEM. Substance Record for SID 184590955. Deposit Date: 2014-06-23. [retrieved on 28 December 2015]. Retrieved from the Internet. <URL: https://pubchem.ncbi.nlm.nih.gov/substance/184590955#section=Top>. entire document	1-4, 8-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 29 December 2015	Date of mailing of the international search report 13 JAN 2016
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/051512

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 18, 22-26
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-4 and 8-17 have been analyzed subject to the restriction that the claims read on the fluorosilicone polymer and up to about 30 weight% of a silica component as described (See first Extra Sheet). The claims are restricted to a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of about 280 m2/g, wherein the material comprises about 27% of the silica component; wherein the fluorosilicone polymer comprises a polymer of formula (I): wherein: n and m are each independently 0; r is 100; each R1 is independently alkyl, wherein R1 is CH3; R2 is haloalkyl, wherein R2 is 3,3,3-trifluoropropyl; R3 is alkyl, wherein R3 is CH3; R4 and R5 are each independently alkyl, wherein the alkyl is CH3; and X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I); wherein the crosslinker is methylhydrosiloxane-dimethylsiloxane copolymer, wherein the crosslinker has a chain length of 5 repeating Si units; wherein the polymeric material having a refractive index of 1.35; wherein the polymeric material having a tensile strength of 500 psi; wherein the polymeric material having a percent elongation of 400%; and wherein the polymeric material having a Young's modulus of 10 psi.

<Continued on first Extra Sheet>

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-4, 8-17

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

<Continued from Box No. III>

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-17 are drawn to polymeric materials.

Group II+: claims 19-21 are drawn to methods thereof.

The first invention of Group I+ is restricted to a polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of about 280 m2/g, wherein the material comprises about 27% of the silica component; wherein the fluorosilicone polymer comprises a polymer of formula (I): wherein: n and m are each independently 0; r is 100; each R1 is independently alkyl, wherein R1 is CH3; R2 is haloalkyl, wherein R2 is 3,3,3-trifluoropropyl; R3 is alkyl, wherein R3 is CH3; R4 and R5 are each independently alkyl, wherein the alkyl is CH3; and X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I); wherein the crosslinker is methylhydrosiloxane-dimethylsiloxane copolymer, wherein the crosslinker has a chain length of 5 repeating Si units; wherein the polymeric material having a refractive index of 1.35; wherein the polymeric material having a tensile strength of 500 psi; wherein the polymeric material having a percent elongation of 400%; and wherein the polymeric material having a Young's modulus of 10 psi. It is believed that claims 1-4 and 8-17 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

The first invention of Group II+ is restricted to a method of making the polymeric material of claim 1, comprising the steps of: (a) combining a vinyl end-capped fluorosilicone polymer with up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m2/g, to obtain a fluorosilicone base composition; (b) adding a crosslinking agent and a curing agent to the fluorosilicone base composition; and (c) curing the fluorosilicone base composition to obtain the polymeric material; wherein the silica component has a surface area of about 280 m2/g, wherein the material comprises about 27% of the silica component; wherein the fluorosilicone polymer comprises a polymer of formula (I): wherein: n and m are each independently 0; r is 100; each R1 is independently alkyl, wherein R1 is CH3; R2 is haloalkyl, wherein R2 is 3,3,3-trifluoropropyl; R3 is alkyl, wherein R3 is CH3; R4 and R5 are each independently alkyl, wherein the alkyl is CH3; and X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I); wherein the crosslinker is methylhydrosiloxane-dimethylsiloxane copolymer, wherein the crosslinker has a chain length of 5 repeating Si units; wherein the polymeric material having a refractive index of 1.35; wherein the polymeric material having a tensile strength of 500 psi; wherein the polymeric material having a percent elongation of 400%; and wherein the polymeric material having a Young's modulus of 10 psi.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. An exemplary election would be a polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of about 280 m2/g, wherein the material comprises about 25% of the silica component; wherein the fluorosilicone polymer comprises a polymer of formula (I): wherein: n and m are each independently 0; r is 100; each R1 is independently alkyl, wherein R1 is CH3; R2 is haloalkyl, wherein R2 is 3,3,3-trifluoropropyl; R3 is alkyl, wherein R3 is CH3; R4 and R5 are each independently alkyl, wherein the alkyl is CH3; and X is a crosslinker which links the polymer of formula (I) with a second polymer of formula (I); wherein the crosslinker is methylhydrosiloxane-dimethylsiloxane copolymer, wherein the crosslinker has a chain length of 5 repeating Si units; wherein the polymeric material having a refractive index of 1.35; wherein the polymeric material having a tensile strength of 500 psi; wherein the polymeric material having a percent elongation of 400%; and wherein the polymeric material having a Young's modulus of 10 psi. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ and II+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I+, polymeric materials, are not present in Group II; and the special technical features of Group II +, methods thereof, are not present in Groups I+.

The Groups I+ and II+ formulae do not share a significant structural element, requiring the selection of alternatives for fluorosilicone polymer and physical properties of silica.

The Groups I+ and II+ share the technical features of a polymeric material comprising a fluorosilicone polymer and up to about 30 weight % of a silica component, wherein the silica component has a surface area of at least about 280 m2/g; a polymeric material comprising a crosslinked dialkyl siloxane-trifluoroalkyl(alkyl)siloxane copolymer, and up to about 30 weight % of a silica component, wherein the silica component has a surface area of at least about 280 m 2/g; a polymeric material comprising a crosslinked dimethyl siloxane-3,3,3-trifluoropropylmethyl siloxane copolymer and up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m 2/g; and a method of making the polymeric material, comprising the steps of: (a) combining a vinyl end-capped fluorosilicone polymer with up to about 30 weight% of a silica component, wherein the silica component has a surface area of at least about 280 m2/g, to obtain a fluorosilicone base composition; (b) adding a crosslinking agent and a curing agent to the fluorosilicone base composition; and (c) curing the fluorosilicone base composition to obtain the polymeric material. However, these shared technical features do not represent a contribution over the prior art.

<Continued on next Extra Sheet>

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Specifically, US 5,171,773 A to Chaffee et al. teach a polymeric material comprising a fluorosilicone polymer and a silica component, wherein the silica component has a surface area of at least about 280 m2/g (Example 1, Col. 3, Ln. 64 through Col. 4, Ln. 55); a polymeric material comprising a crosslinked dialkyl siloxane- trifluoroalkyl(alkyl)siloxane copolymer, and a silica component, wherein the silica component has a surface area of at least about 280 m 2/g (Example 1, Col. 3, Ln. 64 through Col. 4, Ln. 55); and a polymeric material comprising a crosslinked dimethyl siloxane-3,3,3-trifluoropropylmethyl siloxane copolymer and a silica component, wherein the silica component has a surface area of at least about 280 m 2/g (Example 1, Col. 3, Ln. 64 through Col. 4, Ln. 55); a method of making the polymeric material, comprising the steps of: (a) combining a vinyl end-capped fluorosilicone polymer with a silica component, wherein the silica component has a surface area of at least about 280 m2/g, to obtain a fluorosilicone base composition; (b) adding a crosslinking agent and a curing agent to the fluorosilicone base composition; and (c) curing the fluorosilicone base composition to obtain the polymeric material (Example 1, Col. 3, Ln. 64 through Col. 4, Ln. 55).

Additionally, US 5,854,310 A to Maxson teaches a polymeric material comprising a fluorosilicone polymer and up to about 30 weight% of a silica component (Table 1, Col. 6; See component C which contains 25.5 wt. parts of fumed silica).

The inventions listed in Groups I+ and II+ therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.

<End of Box No. III>