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(54) Title of the Invention: **Contact lens formulation and contact lens**
Abstract Title: **Contact lens formulation and contact lens**

(57) A silicone hydrogel contact lens formulation comprises a di-acrylate terminated silicone represented by Formula 1 (see claim 1), a mono-acrylate terminated silicone represented by formula 2 (see claim 1), N-vinyl N-methyl acetamide, hydroxybutyl methacrylate (HOB) and isobornyl methacrylate (IBM). The silicone hydrogel contact lenses are also described.

At least some of the priority details shown above were added after the date of filing of the application.

CONTACT LENS FORMULATION AND CONTACT LENS

[0001] The present invention relates to novel silicone hydrogel contact lens formulations, and an ophthalmic lens, particularly a contact lens and more particularly a silicone hydrogel contact lens comprising the reaction product of a polymerizable composition.

Background

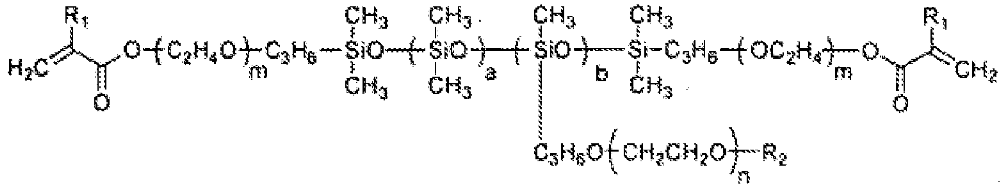
[0002] Silicone hydrogel contact lenses have proven to be acceptable alternatives to hydrogel contact lenses. Contact lens manufacturers are often presented with introducing new contact lenses to satisfy market demand. Thus, there is an ongoing need to develop new silicone hydrogel contact lenses to address this demand.

[0003] In the development of silicone hydrogel contact lenses, it is difficult to predict whether a new silicone hydrogel contact lens formulation will result in clinically acceptable silicone hydrogel contact lenses. Achieving a successful fit, an acceptable level of comfort, an acceptable handling experience, and an acceptable improvement in vision is impacted by various changes in lens chemistry, lens design, and manufacturing processes. For example, changing the formulation of a silicone hydrogel contact lens can alter the oxygen permeability, the water content, the lens surface wettability, and mechanical properties such as modulus, tensile strength, and elasticity. Thus, it is unpredictable as to what combination of chemicals in the formulation will result in desired lens properties.

Summary

[0004] The present invention addresses this ongoing need. The inventors have discovered that when particular combinations of certain polysiloxane compounds of silicone hydrogel contact lens formulations are used, it is necessary to adjust other monomers in the formulations in previously unknown ways, in order to achieve certain desirable contact lens properties. The disclosure herein describes this invention in more detail.

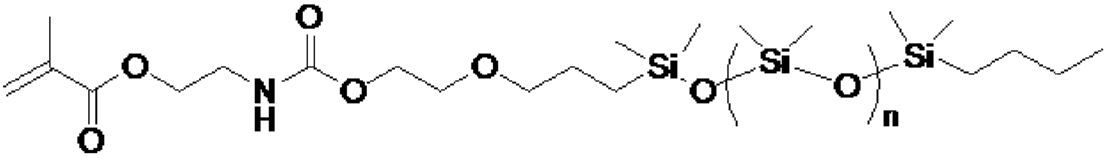
[0005] The applicant has identified that a suitable silicone hydrogel contact lens formulation can be formed using a reaction mixture comprising a silicone component and a silicone-free component. The silicone component comprises, and preferably consists essentially of, two compounds, Formula 1:



$$H_2C{=}C(R_1){-}C({=}O){-}O{-}(C_2H_4O)_m{-}C_3H_6{-}Si(CH_3)_2O{-}(Si(CH_3)_2O)_a{-}(Si(CH_3)(C_3H_6O(CH_2CH_2O)_nR_2)O)_b{-}Si(CH_3)_2{-}C_3H_6{-}(OC_2H_4)_m{-}O{-}C({=}O){-}C(R_1){=}CH_2$$

wherein R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a C_{1-4} hydrocarbon group; m represents an integer of from 0 to 10; n represents an integer of from 4 to 100; a and b represent integers of 1 or more; a+b is from 20 to 500; b/(a+b) is from 0.01 to 0.22, and the configuration of siloxane units includes a random configuration; and

[0006] Formula 2:

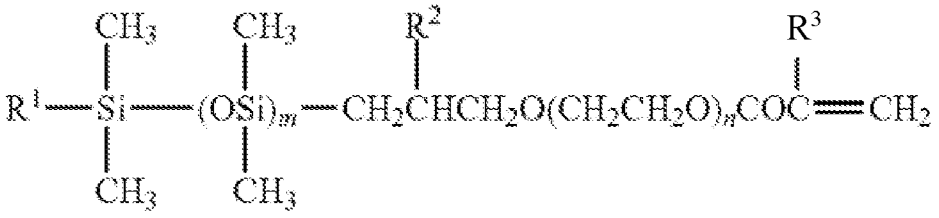


where n is an integer from 10 to 25.

[0007] It is critical that the compound of Formula 1 and the compound of Formula 2 are at a weight ratio of from 50:50 to 80:20. Preferably, the weight ratio of the compound of Formula 1 to the compound of Formula 2 is 53:47 to 77:23.

[0008] In certain embodiments, in the compound of Formula 1, R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a $C_{1\text{-}4}$ hydrocarbon group; m is 0; n represents an integer of from 4 to 15; a represents an integer from 50 to 250, b represents an integer from 5 to 50; and the configuration of siloxane units includes a random configuration, wherein the ratio of a:b is from 5:1 to 30:1, preferably 10:1 to 20:1.

[0009] In an additional embodiment, the silicone component additionally comprises an additional silicone compound of Formula 3:



$$R^1-\underset{CH_3}{\overset{CH_3}{Si}}-(\underset{CH_3}{\overset{CH_3}{OSi}})_m-CH_2\overset{R^2}{C}HCH_2O(CH_2CH_2O)_nCO\overset{R^3}{C}=CH_2$$

wherein m represents an integer of from 3 to 12, n represents an integer from 1 to 10, R^1 is selected from an alkyl group having from 1 to 4 carbon atoms, R^2 is either a hydrogen atom or a methyl group, and R^3 is either a hydrogen atom or a methyl group.

[0010] In some embodiments, in the compound of Formula 3, m is 4, and n is 1, R^1 is a butyl group, R^2 is H, and R^3 is a methyl group.

[0011] Where the compound of Formula 3 is present, it is used in an amount of less than 1% of the total contact lens formulation. In one preferred embodiment of the present formulations, the silicone component consists essentially of Formula 1, Formula 2 and Formula 3.

[0012] The combination of compounds of Formula 1 and Formula 2 advantageously allows a lower amount of silicone component to be used whilst still producing a contact lens which has good oxygen permeability. This also allows for a high water content, which is advantageous for wettability.

[0013] However, when contact lens formulations are produced using the compounds of Formulae 1 and 2, even at these lower amounts, the tensile strength and Young's modulus can be high, as seen in Examples 15 to 17 of US8129442.

[0014] The applicant has identified that it is possible to produce lenses having a tensile strength substantially lower than that seen in formulations containing the compounds of Formula 1 and Formula 2 by focussed selection of the ratios and/or amounts of specific other monomers.

[0015] The silicone-free component comprises an N-vinyl amide component and a methacrylate component.

[0016] The methacrylate component comprises, preferably consists essentially of, and more preferably consists of hydroxybutyl methacrylate (HOB) and isobornyl methacrylate (IBM). It is critical that the HOB and IBM are present in the formulation at a ratio from 60:40 to 90:10.

In a preferred embodiment, the weight ratio of HOB to IBM is from 70:30 to 90:10. In a particularly preferred embodiment, the weight ratio of HOB to IBM is from 85:15 to 90:10, more preferably the ratio is about 88:12. In another embodiment, the weight ratio of HOB to IBM is preferably from 75:25 to 80:20, more preferably about 77:23.

[0017] The N-vinyl amide component comprises N-vinyl N-methyl acetamide (VMA). In some embodiments, the N-vinyl amide component also comprises N-vinyl pyrrolidone (NVP). Where the N-vinyl amide component comprises NVP and VMA, the ratio of NVP to VMA is preferably from 70:30 to 30:70. In preferred embodiments, the N-vinyl amide component consists essentially of and more preferably consists of NVP and VMA.

[0018] It is essential that, if the hydroxybutyl methacrylate to isobornyl methacrylate weight ratio is 60:40 to 65:35 or if the total amount of IBM in the contact lens formulation is greater than 5 weight percent, it is necessary to limit some of the other components further.

[0019] The requirement of at least one, or at least two, or at least three, or at least four, or at least five, or at least six, or all, of the requirements set out below are met.

[0020] In a first aspect of the present invention, the weight ratio of the compound of Formula 1 to the compound of Formula 2 is from 50:50 to 75:25, preferably from 65:35 to 70:30;

[0021] In a second aspect of the present invention, the compound of Formula 2 is present in an amount of at least 12 weight percent;

[0022] In a third aspect of the present invention, the compound of Formula 1 is present in an amount of less than 38 weight percent;

[0023] In a fourth aspect of the present invention, the weight ratio of the compound of Formula 2 to the total of the methacrylate component is greater than 0.9:1;

[0024] In a fifth aspect of the present invention, the weight ratio of compound of Formula 1 to the compound of Formula 2 is less than 3:1; and

[0025] In a sixth aspect of the present invention, the total amount of mono(meth)acrylate compounds in the composition is greater than 26 weight percent.

[0026] One or more of these aspects can be combined. It has been identified that by restricting the range of components as defined in one or more of these aspects, the tensile strength of the resultant lens can be reduced and the lens thereby improved, without negatively impacting on the other lens properties.

[0027] It has been found, surprisingly, that the particular ratio of HOB to IBM, along with the inclusion of VMA, and optionally NVP, results in lenses with desirable properties, particularly a low tensile strength and low Young's modulus compared with previous lenses formed using the combination of the polysiloxane compounds of Formula 1 and Formula 2.

[0028] In a first particularly preferred embodiment, the contact lens formulation comprises a silicone component which consists essentially of Formula 1 and Formula 2, wherein the ratio of Formula 1 to Formula 2 is from 53:47 to 57:43. The N-vinyl amide component consists essentially of NVP and VMA, wherein the ratio of NVP:VMA is from 68:32 to 72:28. The methacrylate component consists essentially of HOB and IBM, wherein the ratio of HOB to IBM is from 85:15 to 90:10. It is preferred that the silicone component is from 45 to 55 weight percent of the formulation. It is further preferred that the methacrylate component is from 10 to 20 weight percent of the formulation. It is yet further preferred that the N-vinyl amide component is from 30 to 40 weight percent of the formulation.

[0029] In a second particularly preferred embodiment, the contact lens formulation comprises a silicone component which consists essentially of Formula 1 and Formula 2, wherein the ratio of Formula 1 to Formula 2 is from 73:27 to 77:23. The N-vinyl amide component consists essentially of NVP and VMA, wherein the ratio of NVP:VMA is from 32:68 to 28:72. The methacrylate component consists essentially of HOB and IBM, wherein the ratio of HOB to IBM is from 85:15 to 90:10. It is preferred that the silicone component is from 45 to 55 weight percent of the formulation. It is further preferred that the methacrylate component is from 10 to 20 weight percent of the formulation. It is yet further preferred that the N-vinyl amide component is from 30 to 40 weight percent of the formulation.

[0030] In a third particularly preferred embodiment, the contact lens formulation comprises a silicone component which consists essentially of Formula 1, Formula 2 and Formula 3, wherein Formula 3 is present in an amount of less than 0.6 weight percent of the formulation, wherein the ratio of Formula 1 to Formula 2 is from 60:40 to 65:35. The N-vinyl amide component consists essentially of VMA. The methacrylate component consists essentially of HOB and IBM, wherein the ratio of HOB to IBM is from 75:25 to 80:20. It is preferred that the silicone component is from 45 to 55 weight percent of the formulation. It is further preferred that the methacrylate component is from 5 to 15 weight percent of the formulation. It is yet further preferred that the N-vinyl amide component is from 30 to 40 weight percent of the formulation.

[0031] Preferably the formulation further comprises at least one of: a photoinitiator, a thermal initiator; a crosslinking monomer; a UV blocker; and a tinting agent.

[0032] In another embodiment of the invention, a silicone hydrogel contact lens comprising the polymerized reaction product of the formulation of any preceding embodiment is disclosed.

[0033] The silicone hydrogel contact lens may have a tensile strength from 0.4 MPa to 1.0 MPa. The silicone hydrogel contact lens typically has a tensile strength less than or equal to 1.0 MPa, and preferably less than or equal to 0.9 MPa. The silicone hydrogel contact lens typically has a tensile strength of at least 0.4 MPa, and more preferably at least 0.5 MPa. In at least some preferred embodiments, the silicone hydrogel contact lens has a tensile strength from 0.5 MPa to 0.9 MPa.

[0034] The silicone hydrogel contact lens can have a sessile drop contact angle less than 30 degrees, more preferably less than 25 degrees.

[0035] The silicone hydrogel contact lens can have an equilibrium water content from 45 to 55 wt%.

[0036] The silicone hydrogel contact lens can have an oxygen permeability of greater than 100 barrers, preferably greater than 110 barrers, more preferably greater than 120 barrers, and especially from 110 to 140 barrers.

[0037] The silicone hydrogel contact lens can have a Young's modulus less than or equal to 1.1 MPa, preferably less than or equal to 1.0 MPa. The Young's modulus is preferably at least 0.3 MPa, more preferably at least 0.5 MPa. A preferred range is from 0.5 MPa to 0.95 MPa.

[0038] The silicone hydrogel contact lens can have a chord diameter from 13.5 to 15.5 mm and a base curve from 7.5 to 9.5 mm. The skilled person is aware of other suitable chord diameters and base curves.

Detailed description

[0039] Silicone hydrogel contact lenses are described herein that have good dimensional stability, are ophthalmically-acceptable, and can be manufactured without the use of volatile organic solvents or diluents in the formulations. The silicone hydrogel contact lenses comprise a polymeric lens body that is the reaction product of a polymerizable composition or silicone hydrogel contact lens formulation comprising a silicone component and a silicone-free component. The silicone component comprises, or consists essentially of two compounds, Formula 1 and Formula 2. It is critical that the compound of Formula 1 and the compound of Formula 2 are at a ratio of from 50:50 to 80:20.

[0040] References herein to 'at least one' of a type of ingredient refer to both a) a single ingredient, and b) a combination of two or more ingredients of the same type.

[0041] Throughout this disclosure, references to ‘a total amount’ of a particular component (i.e., a combination of two or more ingredients of the same type) in a polymerizable composition refer to the sum of the amounts of all ingredients of the same type.

[0042] The following definitions for the quoted terms provided below are applicable herein unless context dictates otherwise:

[0043] A “monomer” refers to any molecule capable of reacting with other molecules that are the same or different, to form a polymer or copolymer. Thus, the term encompasses polymerizable pre-polymers and macromers, there being no size-constraint of the monomer unless indicated otherwise.

[0044] A “siloxane monomer” contains at least one Si—O group, and is typically either “mono-functional” or “multi-functional”, meaning that it has either one polymerizable group or two or more polymerizable groups, respectively. A “non-siloxane monomer” is a monomer that does not contain any Si—O groups.

[0045] A “silicone component” is a component or portion of the silicone hydrogel contact lens formulation which is composed of all of the siloxane monomers.

[0046] A “silicone-free component” is a component or portion of the silicone hydrogel contact lens formulation which is composed of all of the non-siloxane monomers

[0047] An “N-vinyl amide component” is a component or portion of the silicone-free component of the silicone hydrogel contact lens formulation which is composed of at least one non-siloxane monomer that has a vinyl group bound directly to a nitrogen atom.

[0048] A “methacrylate component” is a component or portion of the silicone-free component of the silicone hydrogel contact lens formulation which is composed of at least one non-siloxane monomer that has a single polymerizable methacrylate group.

[0049] A “(meth)acrylate-containing monomer” is any non-siloxane monomer that has a single polymerizable (meth)acrylate group (e.g., methyl methacrylate, etc.). A siloxane monomer having at least one polymerizable (meth)acrylate group is referred to herein as a “(meth)acrylate-containing siloxane monomer”. “(Meth)acrylate” covers both methacrylate groups and acrylate groups. Where only methacrylate or acrylate is covered, it will be referred to explicitly.

[0050] “Consists of” means that a formulation or component contains only the listed components, compounds, or monomers.

[0051] “Consists essentially of” means that a formulation or component contains the listed compounds or monomers but can also contain other monomers or compounds which fall within the definition of that formulation or component such as dimeric or polymeric impurities. These additional monomer or compounds can be present in an amount which does not have an impact on the final lens formulation. Additional monomers or reactive entities can be present in an amount of less than 5%, 2%, 1%, 0.5% or 0.1% based on the total amount of the specific formulation or component.

[0052] A “polymerizable composition” is a composition comprising polymerizable ingredients, where the composition has not yet been subjected to conditions that result in polymerization of the polymerizable ingredients. Thus, the present silicone hydrogel contact lens formulations are considered polymerizable compositions.

[0053] In the case of polyorganosiloxane prepolymers, and other polydisperse monomers, the term “molecular weight”, as used herein, refers to the absolute number average molecular weight Mn (in units of Daltons (Da) or g/mol) of the monomer. The number average molecular weight is typically determined using GPC, using polystyrene standards. In addition, the number average molecular weight may be determined by identification of the number average molecular weight on a technical data sheet or specification sheet provided by a chemical supplier to a contact lens manufacturer.

[0054] In the present disclosure, where a value is given for repeat groups in a structural formula, such as Formula 1, Formula 2 or Formula 3, it is an average value. The skilled person would understand that a complex molecule of this kind contains a mixture of components.

[0055] As used herein, the term “total formulation” or “total contact lens formulation” refers to all formulation ingredients excluding diluents and/or solvents that are not incorporated into the final polymeric contact lens material. It can be understood that when a weight percent of an ingredient of the total formulation is provided, it refers to the weight percent of that ingredient based on the total weight of the formulation.

[0056] Throughout this disclosure, a reference to “an example” or “a specific example” or similar phrase, is intended to introduce a feature or features of the contact lens, polymerizable composition, or method of manufacture (depending on context) that can be combined with any combination of previously-described or subsequently-described examples (i.e. features), unless a particular combination of features is mutually exclusive, or if context indicates otherwise.

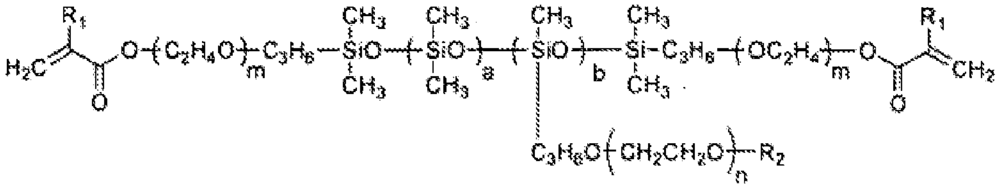
[0057] Throughout this disclosure, when a series of lower limit ranges and a series of upper limit ranges are provided, all combinations of the provided ranges are contemplated as if each combination were specifically listed. Also, throughout this disclosure, when a series of values is presented with a qualifier preceding the first value, the qualifier is intended to implicitly precede each value in the series unless context dictates otherwise. For example, for the values listed above, it is intended that the qualifier “from about” implicitly precedes the ratio of 50:50, and that the qualifier “to about” implicitly precedes the ratio 80:20.

[0058] As used herein, unless specified otherwise, ratio refers to weight ratio. As used herein, weight ratio refers to the ratio between the weight of a first component and the weight of a second component in the formulation.

[0059] A silicone hydrogel contact lens formulation, comprising a silicone component; and a silicone-free component is disclosed herein.

[0060] The silicone component comprises, or consists essentially of, or in some embodiments consists of, a bi-functional (meth)acrylate-containing siloxane monomer and a mono-functional methacrylate-containing siloxane monomer.

[0061] The bi-functional (meth)acrylate-containing siloxane monomer is represented by Formula 1:



$$H_2C{=}C(R_1){-}C({=}O){-}O{-}(C_2H_4O)_m{-}C_3H_6{-}Si(CH_3)_2O{-}\left(Si(CH_3)_2O\right)_a{-}\left(Si(CH_3)(C_3H_6O(CH_2CH_2O)_nR_2)O\right)_b{-}Si(CH_3)_2{-}C_3H_6{-}(OC_2H_4)_m{-}O{-}C({=}O){-}C(R_1){=}CH_2$$

wherein R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a $C_{1\text{-}4}$ hydrocarbon group; m represents an integer of from 0 to 10; n represents an integer of from 4 to 100; a and b represent integers of 1 or more; a+b is from 20-500; b/(a+b) is from 0.01-0.22, and the configuration of siloxane units includes a random configuration.

[0062] The bi-functional (meth)acrylate-containing siloxane monomer of Formula 1 can have an average molecular weight Mw of at least 8,000, 10,000, 12,000 or 15,000 Da. The bi-functional (meth)acrylate-containing siloxane monomer of Formula 1 can have an average molecular weight Mw of less than 25,000, 20,000 12,000, 11,000, 10,000 or 9,000 Da. Preferably, the bi-functional (meth)acrylate-containing siloxane monomer has an average molecular weight Mw of from 8,000 to 20,000 Da. In one preferred embodiment, the bi-functional (meth)acrylate-containing siloxane monomer of Formula 1 has an average molecular weight Mw of from 8,000 to 11,000 Da. In another preferred embodiment, the bi-functional (meth)acrylate-containing siloxane monomer of Formula 1 has an average molecular weight Mw of from 15,000 to 20,000 Da.

[0063] In certain embodiments, in the compound of Formula 1, R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a C1-4 hydrocarbon group; m is 0; n represents an integer of from 4 to 15; a represents an integer from 50 to 250, b represents an integer from 5 to 50; and the configuration of siloxane units includes a random configuration, wherein the ratio of a:b is from 5:1 to 30:1, preferably 10:1 to 20:1.

[0064] It is preferred that R_1 is a methyl group. It is preferred that R_2 is H or a methyl group, and more preferably a methyl group. It is additionally preferred that m is 0. It is preferred that n is from 6 to 9.

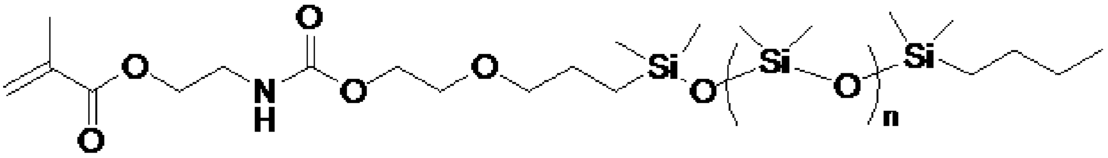
[0065] In one preferred embodiment, a is from 60 to 100, more preferably from 70 to 80, and b is from 4 to 8, more preferably from 5 to 8. It is further preferred that R_1 is methyl, R_2 is methyl, m is 0 and n is from 7 to 8.

[0066] A particularly preferred bi-functional (meth)acrylate-containing siloxane monomer has a CAS Registry Number of: 1216820-69-7.

[0067] In another preferred embodiment, a is from 140 to 220, more preferably from 150 to 200, and b is from 8 to 15, more preferably from 9 to 13. It is further preferred that R_1 is methyl, R_2 is methyl, m is 0 and n is from 7 to 8.

[0068] Methods of making compounds of Formula 1 are described in US. Patent no. 8,129,442 (incorporated herein by reference).

[0069] The mono-functional methacrylate-containing siloxane monomer is represented by Formula 2:



where n is an integer from about 10 to 25, preferably from 13 to 18.

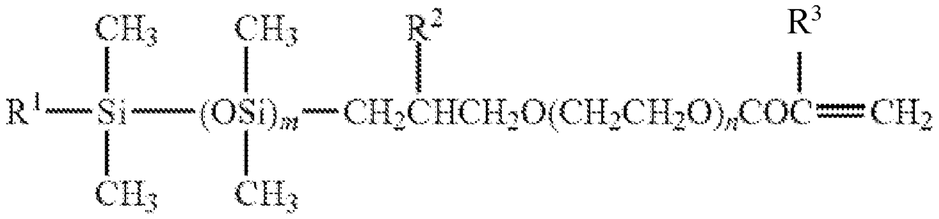
[0070] The mono-functional methacrylate-containing siloxane monomer of Formula 2 has an average molecular weight of less than 2,000, preferably less than 1,800 Da, and greater than 800, preferably greater than 1,000 Da. In a further specific example, the mono-functional methacrylate-containing siloxane monomer may have an average molecular weight of from 1,000 to 1,800 Da.

[0071] Preferably, the mono-functional methacrylate-containing siloxane monomer has a CAS registry number of 697234-76-7.

[0072] Siloxane monomers of Formula 2 are described in US. Pat. No. 6,310,169 (incorporated herein by reference).

[0073] The compound of Formula 1 and the compound of Formula 2 are at a weight ratio of from 50:50 to 80:20. In one preferred embodiment, the weight ratio of the compound of Formula 1 to the compound of Formula 2 is from 53:47 to 77:23. In some particular embodiments the weight ratio is from 52:48 to 58:42. In some particular embodiments, the weight ratio is from 60:40 to 65:35. In some particular embodiments the weight ratio is from 70:30 to 77:23. In some particular embodiments, the weight ratio is about 55:45, about 63:37 or about 75:25.

[0074] In an additional embodiment, the silicone component comprises an additional silicone compound, which is a mono-functional (meth)acrylate-containing siloxane monomer of Formula 3:



$$R^1-\underset{CH_3}{\overset{CH_3}{|}}{\underset{|}{\overset{|}{Si}}}-(O\underset{CH_3}{\overset{CH_3}{Si}})_m-CH_2\overset{R^2}{C}HCH_2O(CH_2CH_2O)_nCO\overset{R^3}{C}=CH_2$$

wherein m represents an integer of from 3 to 12, n represents an integer from 1 to 10, R^1 is selected from an alkyl group having from 1 to 4 carbon atoms, and each of R^2 and R^3 of Formula 3 is independently selected from a hydrogen atom or a methyl group.

[0075] In some embodiments, in the compound of Formula 3, m is 4, and n is 1. It is further preferred that R^1 is a butyl group, R^2 is H, and R^3 is a methyl group.

[0076] Where the compound of Formula 3 is present, it is used in an amount of less than 1 weight percent, preferably less than 0.8 weight percent, more preferably less than 0.6 weight percent of the total contact lens formulation. In one preferred embodiment of the present formulations, the silicone component consists essentially, preferably consists of Formula 1, Formula 2 and Formula 3.

[0077] In some embodiments, the weight percent of the silicone component is greater than 48%, 48.5%, or 49%. In some embodiments the weight percent of the silicone component is less than 53%, 52.5%, 52%, 51.5%, 51%, or 50.5%. In some embodiments any one of the lower limits of the weight percent of the silicone component is combined with any one of the upper limits of the weight percent of the silicone component. For example, the silicone component can be present in the formulation from 48% (wt/wt) to 53% (wt/wt), preferably from 48% to 51%.

[0078] In another preferred embodiment, it is preferred that the amount of the compound of Formula 2 is greater than 12 weight percent of the total composition. It is further preferred that the amount of the compound of Formula 2 is less than 25 weight percent. For example, the compound of Formula 2 can be present in the formulation from 12 to 25 % (wt/wt).

[0079] In another preferred embodiment, it is preferred that the amount of the compound of Formula 1 is less than 38 weight percent. It is further preferred that the amount of the compound of Formula 1 is greater than 26 weight percent. For example, the compound of Formula 1 can be present in the formulation from 26 to 38 % (wt/wt).

[0080] It is particularly preferred that the amount of the compound of Formula 2 is greater than 12 weight percent and the amount of the compound of Formula 1 is less than 38 weight percent.

[0081] In addition, it can be understood that the silicone component of the present formulations is free of a hydroxy-functionalized siloxane compound, is free of TRIS, or is free of both.

[0082] The silicone-free component comprises an N-vinyl amide component (c); and a methacrylate component (d).

[0083] The N-vinyl amide component comprises N-vinyl N-methyl acetamide (VMA). The N-vinyl amide component optionally further comprises N-vinyl pyrrolidone (NVP). It is further preferred that the N-vinyl amide component consists essentially of, and preferably consists of NVP and VMA.

[0084] In one preferred embodiment, where the N-vinyl amide component includes both NVP and VMA, the ratio of NVP to VMA is from 70:30 to 30:70. In some embodiments the ratio is about 70:30. In some embodiments the ratio is about 30:70. In a further specific example, the polymerizable composition has a weight ratio of total amount of N-vinyl amide component to total amount of (meth)acrylate-containing siloxane monomer (i.e. the mono- and bi-functional (meth)acrylate-containing siloxane monomers) of from about 40:60 to 45:55. It is further preferred that the ratio is from 41:59 to 42:58.

[0085] In some embodiments, the weight percent of the N-vinyl amide component is greater than 34%, or 34.5%. In some embodiments the weight percent of the N-vinyl amide component is less than 40%, 39%, 37% or 36.5%. In some embodiments any one of the lower limits of the weight percent of the N-vinyl amide component is combined with any one of the upper limits of the weight percent of the N-vinyl amide component. In some embodiments the weight percent of the N-vinyl amide component is between 34.5% and 35.5%.

[0086] In one preferred embodiment, the N-vinyl amide component consists essentially of, and preferably consists of VMA. In a further specific example, the polymerizable composition has a weight ratio of total amount of N-vinyl amide component to total amount of (meth)acrylate-containing siloxane monomer (i.e., the mono- and bi-functional (meth)acrylate-containing siloxane monomers) of from about 40:60 to 45:55. It is further preferred that the ratio is from 44:56 to 45:55.

[0087] Where the N-vinyl amide component consists essentially of, or consists of VMA, the weight percent of the N-vinyl amide component is greater than 35%, or 38%. The weight percent of the N-vinyl amide component is less than 40% or 39%. In some embodiments any one of the lower limits of the weight percent of the N-vinyl amide component is combined with any one of the upper limits of the weight percent of the N-vinyl amide component. In some embodiments the weight percent of the N-vinyl amide component is between 38% and 39%.

[0088] In another specific example, the total amount of the compound of Formula 2 and the N-vinyl amide component is at least 47 weight percent, preferably at least 50 weight percent. The total amount of the compound of Formula 2 and the N-vinyl amide component is less than 70 weight percent, preferably less than 60 weight percent.

[0089] The methacrylate component (d) comprises, and in some embodiments consists essentially of, and in some embodiments consists of, hydroxybutyl methacrylate (HOB) and isobornyl methacrylate (IBM), wherein the hydroxybutyl methacrylate and isobornyl methacrylate are present in the formulation at a weight ratio from 60:40 to 90:10. In some embodiments, the ratio of HOB to IBM is greater than 65:35, 70:30, 75:25, 80:20, 85:15, or 87:13. In some embodiments, the ratio of HOB to IBM is less than 90:10, 89.5:10.5, 89:11, or 88.5:11.5. In some embodiments any one of the lower limits of ratio of HOB to IBM is combined with any one of the upper limits of the ratio of HOB to IBM. In some embodiments, the ratio of HOB to IBM is between 85:15 and 90:10 or is about 88:12.

[0090] Other silicone-free methacrylate-containing monomers are known in the field and can be present in the contact lens formulation. Exemplary silicone-free methacrylate-containing monomers include methyl methacrylate (MMA), tert butyl methacrylate (tBMA), 2-hydroxyethyl methacrylate (HEMA), ethylene glycol methyl ether methacrylate (EGMA), and combinations thereof. A preferred additional silicone-free methacrylate-containing monomer is methyl methacrylate (MMA).

[0091] It is preferred that these additional methacrylate-containing monomers are present in a total amount of less than 5%, more preferably less than 3% by weight, yet more preferably less than 1 % by weight of the contact lens formulation and even more preferably in the minor amounts as defined above where the methacrylate component consists essentially of HOB and IBM. It is particularly preferred that there are no other methacrylate-containing monomers.

[0092] Where the ratio of HOB to IBM is from 60:40 to 65:35 or where the total amount of IBM is greater than 5 weight percent, it is preferred in one embodiment that the ratio of the compound of Formula 1 to the compound of Formula 2 is less than or equal to 3:1, preferably from 50:50 to 75:25, more preferably from 65:35 to 70:30.

[0093] In another preferred embodiment, it is preferred that the amount of the compound of Formula 2 is greater than 12 weight percent of the total composition. This is particularly the case where the ratio of HOB to IBM is from 60:40 to 65:35 or where the total amount of IBM is greater than 5 weight percent. It is further preferred that the amount of the compound of Formula 2 is less than 25 weight percent.

[0094] In another preferred embodiment, it is preferred that the amount of the compound of Formula 1 is less than 38 weight percent. This is particularly the case where the ratio of HOB to IBM is from 60:40 to 65:35 or where the total amount of IBM is greater than 5 weight percent. It is further preferred that the amount of the compound of Formula 1 is greater than 26 weight percent.

[0095] It is particularly preferred that the amount of the compound of Formula 2 is greater than 12 weight percent and the amount of the compound of Formula 1 is less than 38 weight percent.

[0096] In a specific example, the polymerizable composition may have a weight ratio of compound of Formula 2 to total amount of non-siloxane methacrylate-containing monomer of greater than 0.9:1, preferably greater than 1:1. This is particularly the case where the ratio of HOB to IBM is from 60:40 to 65:35 or where the total amount of IBM is greater than 5 weight percent.

[0097] In another specific example, the total amount of mono-functional methacrylate-containing non-silicone and siloxane monomers, collectively is greater than 26 weight percent, and preferably greater than 30 weight percent. This is particularly the case where the ratio of HOB to IBM is from 60:40 to 65:35 or where the total amount of IBM is greater than 5 weight percent.

[0098] Typically, the formulation further comprises one or more additional components which are common in contact lens formulations. Suitable additional components include a photoinitiator, a thermal initiator, a cross-linking agent, UV blockers and a tinting agent.

[0099] The polymerizable composition may additionally comprise at least one non-siloxane cross-linking agent. As used herein, a “cross-linking agent” is any compound having a molecular weight of less than about 2,000 Da. with two or more ethylenically unsaturated groups. Thus, a cross-linking agent can react with functional groups on two or more polymer chains so as to bridge one polymer to another. TAIC is particularly preferred as the cross-linker in the formulations of the present invention.

[00100] The cross-linker is preferably used in an amount of from 0.03 to 0.2 weight percent of the contact lens formulation.

[00101] The composition additionally can comprise one or more tinting agents. Preferred tinting agents are reactive tinting agents and particularly tinting agents identified as “Reactive Blue” dyes.

[00102] The composition can additionally comprise one or more UV blockers.

[00103] Contact lenses can be made from the polymerizable compositions described herein using curing and other processing methods known in the field, such as cast molding, spin casting, injection molding, forming a polymerized rod that is subsequently lathed, etc. In a specific example, the polymerizable composition is cast molded between molds formed of a thermoplastic polymer. The thermoplastic polymer is typically a non-polar material, such as polypropylene, but polar mold materials, such as ethylene vinyl alcohol, are also used in the field. Briefly, a first mold member defining the front surface of the contact lens, referred to as a “female mold member”, is filled with an amount of the polymerizable composition sufficient to form a single polymeric lens body. A second mold member defining the back (i.e. eye-contacting) surface of the contact lens, referred to as the "male mold member", is coupled to the female mold member to form a mold assembly having a lens-shaped cavity with the amount of polymerizable composition therebetween

[00104] The polymerizable composition within the contact lens mold assembly is polymerized using any suitable curing method. Typically, the polymerizable composition is exposed to polymerizing amounts of heat or ultraviolet light (UV). In the case of UV-curing, also referred to as photopolymerization, the polymerizable composition typically comprises a photoinitiator such as benzoin methyl ether, 1-hydroxycyclohexylphenyl ketone, Darocur or Irgacur (available from Ciba Specialty Chemicals). Photopolymerization methods for contact lenses are described in U.S. Pat. No. 5,760,100 incorporated herein by reference. In the case of heat-curing, also referred to as thermal curing, the polymerizable composition typically comprises a thermal initiator. Exemplary thermal initiators include 2,2′-azobis(2,4-dimethylpentanenitrile) (VAZO-52), 2,2′-Azobis(2-methylpropanenitrile) (VAZO-64), and 1,1′-azo bis(cyanocyclohexane) (VAZO-88). The contact lens mold assemblies containing the contact lens formulations are cured by exposing the contact lens mold assemblies to heat or UV light for a time ranging from about 1 hour to about 5 hours. Additional thermal polymerization methods for contact lenses are described in US Publ. no. 2007/0296914 and U.S. Pat. No. 7,854,866, incorporated herein by reference.

[00105] At the completion of curing, the polymerized material between the mold members of the mold assembly has the shape of a contact lens, and is referred to herein as a "polymeric lens body". The male and female mold members are demolded, i.e. separated, and the polymeric lens body is removed, i.e. delensed, from the mold member to which it is adhered. These processes are referred to as demolding and delensing, respectively, and a variety of such methods are known to those of ordinary skill in the field. In some methods, the demolding and delensing processes can comprise a single process step, such as when the molds are separated using a liquid which also removes the polymeric lens body from the mold. In other methods, such as when a dry-demolding process is used, the polymeric lens body typically remains on one of the mold members and is delensed in a subsequent process step. Delensing can also be a wet or dry process. In one example, delensing is carried out by a "float off" method in which the mold member to which a polymeric lens body is adhered is immersed in water. The water may optionally be heated (e.g. up to about 100° C.). Typically, the polymeric lens bodies float off of the mold members in about ten minutes. Dry delensing can be carried out manually, for example using tweezers to remove the polymeric lens bodies from the mold member, or they can be removed using an automated mechanical process, such as described in U.S. Pat. No. 7,811,483 (incorporated herein by reference). Additional demolding and delensing methods for silicone hydrogel contact lenses are described in US Publ No. 2007/0035049 (incorporated herein by reference).

[00106] After delensing, the polymeric lens body is washed to remove unreacted or partially reacted ingredients from the polymeric lens body and to hydrate the polymeric lens body. For example, the contact lenses can be exposed to organic solvents, such as ethanol, isopropyl alcohol, industrial methylated spirts, and the like, or water, or mixtures thereof. Exemplary washing methods are described in US Pat. Publ. No. 2007/0296914 (incorporated herein by reference) and in Example 1 below.

[00107] After washing, the hydrated polymeric lens body is typically placed into a blister package, glass vial, or other appropriate container, all referred to herein as "packages." A packaging solution is also added to the container, which is typically a buffered saline solution such as phosphate- or borate-buffered saline. The packaging solution may optionally contain additional ingredients such as a comfort agent, a hydrophilic polymer, a surfactant or other additive that prevents the lens from sticking to the container, etc. The package is sealed, and the sealed polymeric lens body is sterilized by autoclaving. The final product is a sterile, packaged ophthalmically-acceptable contact lens.

[00108] In any of the above-described examples, the contact lens may be characterized by one or more of the following properties: contact angle, oxygen permeability, tensile strength, Young's modulus, and equilibrium water content, as detailed below.

[00109] In any of the below-described examples, the contact lens may have a contact angle of less than about 30°, or 25°, where the contact angle is the static advancing contact angle as determined using a sessile drop method. To determine the contact angle of a contact lens surface, contact lenses to be tested are soaked in phosphate buffered solution (PBS) for at least 12 hours. Using rubber tipped tweezers, the lenses are removed from the PBS and shaken to remove excess water. A 4 mm diameter section of each lens is cut with a lens cutter. The surface of the contact lens section to be tested is blotted dried by placing it face down on a microscope lens wipe and gently dragging the lens section across the wipe using rubber tipped tweezers until no liquid is observed absorbing into the wipe. The lens section is placed on a microscope slide, ensuring that it lies flat with the blotted surface facing upwards. Measurements are taken promptly to ensure that the lens section does not become dry (as evidenced by deformation of the lens section). In the Krüss DSA-100, the Drop Shape Analysis program is turned on and the "Sessile drop (VCA eq)" method is selected with the following settings: camera tilt=+2; 100 µl syringe with straight needle; dispense solution=purified water; dispense volume=0.75 µl; dispense speed=7.5 µl/min; and dispense mode=volume. The microscope slide is placed on the sample stage so that the longer side of the lens section is perpendicular to the camera. The syringe is moved to fit in the viewing screen and the image is adjusted until a maximum is reached in the median window. The water is dispensed onto the lens. Between 10 to 15 seconds after dispensing the water, the image of the drop is captured. A calculation method is selected according to the contact angle as follows: <30°=Circle Fitting Method, 30°-130°=Tangent Method−1; >130°=Tangent Method−2. The average contact angle measurement of 5 lens sections is taken to be the contact angle for the particular surface (i.e. posterior or anterior) of the contact lens.

[00110] For oxygen permeability, the Dk values provided in the Examples below were determined using a Rehder 201T Oxygen Permometer/polarographic cell following the polarographic method described in ISO18369-4:2017 section 4.4.3.

[00111] In any of the below-described examples, the contact lens may have a Young's modulus (i.e. tensile modulus) of at least 0.3 MPa or 0.5 MPa, to 0.95 MPa, 1.0 MPa or 1.1 MPa. In preferred embodiments, the contact lens has a Young's modulus from 0.3 MPa to 1.1 MPa, and preferably from 0.5 to 0.95 MPa.

[00112] The contact lenses have a tensile strength of less than or equal to 1.0 MPa, preferably less than or equal to 0.9 MPa. The contact lens typically has a tensile strength of at least 0.4 MPa, more preferably at least 0.5 MPa. Preferred embodiments of the present contact lenses have a tensile strength from 0.5 MPa to 0.9 MPa.

[00113] The modulus, elongation, and tensile strength values reported herein were determined using an Instron Model 3342, 3343, or 5944 mechanical testing system (Instron Corporation, Norwood, Mass., USA) and Bluehill Materials Testing Software, using a custom-built rectangular contact lens cutting die with 4 mm spacing to prepare the rectangular sample strip. The modulus was determined inside a chamber having a relative humidity of least 70%. A lens was soaked in phosphate buffered solution (PBS) for at least 10 minutes prior to testing. While holding the lens concave side up, a central strip of the lens was cut using the cutting die. The thickness of the strip was determined using a calibrated gauge (Rehder electronic thickness gauge, Rehder Development Company, Castro Valley, Calif., USA). Using tweezers, the strip was loaded into the grips of the calibrated Instron apparatus, with the strip fitting over at least 75% of the grip surface of each grip. A test method designed to determine the maximum load

(N), the tensile strength (MPa), the strain at maximum load (% elongation) and the mean and standard deviation of the tensile modulus (MPa) was run, and the results were recorded.

[00114] In any of the above-described examples, the contact lens may have an equilibrium water content (EWC) of at least about 30 wt. %, 40 wt. % or 45 wt. % and up to about 50 wt%, 55 wt%, 60 wt. % or 70 wt. %. For example, the contact lens may have an EWC from 40 to 60 wt%. To measure EWC, excess surface water is wiped off the lens and the lens is weighed to obtain the hydrated weight. The lens is dried in an oven at 105° C, and weighed. The weight difference is determined by subtracting the weight of the dry lens from the weight of the hydrated lens. The wt. % EWC of the lens is = (weight difference/hydrated weight)×100. In a specific example, the contact angle is ≦30° and the equilibrium water content is most preferably at least 45 wt. % and up to 55 wt%.

[00115] As is evident from the disclosure of the application as a whole, including the claim structure and the specific examples, the exemplary components of the polymerizable composition disclosed herein are typically combined in embodiments of the invention. For example, the person skilled in the art would recognize that the polymerizable composition of the invention advantageously includes the exemplary mono-functional (meth)acrylate-containing siloxane monomers disclosed herein in combination with the exemplary bi-functional (meth)acrylate-containing siloxane monomers disclosed herein and in combination with the exemplary N-vinyl amide components disclosed herein and in combination with the exemplary (meth)acrylate components disclosed herein.

[00116] As demonstrated by the specific examples, it has been found that combinations of the preferred mono-functional methacrylate-containing siloxane monomers, bi-functional (meth)acrylate-containing siloxane monomers, N-vinyl amide component, and methacrylate-containing monomers of the invention provide contact lenses of the invention with advantageous properties such as reduced tensile strength.

EXAMPLES

[00117] The following Examples illustrate certain aspects and advantages of the present invention, which should be understood not to be limited thereby. The reactants used in the Examples are detailed in Table 1, the particular amounts of each component used are set out in Table 2 as weight percents of the total formulation, ratios and combined totals of components are presented in Table 3 and the properties are presented in Table 4.

[00118] The silicone hydrogel lenses of Examples 1 to 6 and Comparative Examples were produced according to the following method.

[00119] The compounds or monomers were all mixed and stirred to form a polymerizable composition or a silicone hydrogel contact lens formulation.

[00120] The formulation was put in a mold for a contact lens.

[00121] The lenses were either cured using ultraviolet light for about 1 hour (Examples 1 and 2 and Comparative Examples) or heat for about 5 hours (Example 3). The skilled person is aware of suitable methods for curing contact lens formulations.

[00122] The cured polymers were removed from the contact lens molds and washed to remove unreacted materials by contacting them with organic solvent, water, or combinations thereof, and then the washed contact lenses were placed in a package and sterilized in an autoclave to provide a sterilized packaged contact lens. The contact lenses of all Examples and Comparative Examples were transparent and flexible, and also had good water wettability.

Table 1

Abbreviation	Compound
Si-1	Formula 1 above wherein R_1 is a methyl group, R_2 is a methyl group, m is 0, a is 60-100, b is 4-7, n is 6-8.
Si-1a	Formula 1 above wherein R_1 is a methyl group, R_2 is a methyl group, m is 0, a is 120-230, b is 6-15, and n is 6-8.
Si-2	Formula 2 above wherein n is 16.
Si-3	Formula 3 above wherein R^1 is a butyl group, R^2 is hydrogen, and R^3 is a methyl group, and n is 1, and m is 5.
VMA	N-vinyl-N-methylacetamide [CAS# 3195-78-6]
NVP	N-vinyl pyrrolidone [CAS# 88-12-0]
HOB	Hydroxybutyl methacrylate [CAS# 29008-35-3]
IBM	Isobornyl methacrylate [CAS# 7534-94-3]
TAIC	Triallyl isocyanurate [CAS# 1025-15-6]
TPP	Triphenylphosphine [CAS# 603-35-0]
TPO	Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide [CAS# 75980-60-8]
AIBN	Azobisisobutyronitrile [CAS # 78-67-1]
AOT	Sodium bis(2-ethylhexyl)sulfosuccinate (sodium dioctyl sulfosuccinate) [CAS# 577-11-7]
AE	2-Allyloxyethanol [CAS # 111-45-5]

Table 2

	Example 1	**Example 2**	**Comparative Example 1**	**Comparative Example 2**	**Example 3**	**Example 4**	**Example 5**	**Example 6**
Ingredient								
TAIC	0.09	0.09	0.10	0.10	0.10	0.12	0.12	0.05
IBM	1.87	1.65	5.40	5.40	5.40	3.40	1.40	2.08
HOB	13.73	12.07	9.00	9.00	9.00	11.00	9.00	6.92
VMA	10.42	24.70	9.00	7.00	7.00	9.00	9.00	38.72
NVP	24.30	10.58	27.10	27.10	27.10	27.10	27.10	
Si-1	26.97	37.76						30.15
Si-1a			39.80	39.80	34.80	37.78	41.78	
Si-2	22.07	12.59	9.00	11.00	16.00	11.00	11.00	17.99
Si-3								0.49
AE								0.63
Reactive dye	0.01	0.01						0.01
TPO	0.09	0.09	0.10	0.10	0.10	0.10	0.10	
AIBN								0.45
TPP								0.40
AOT	0.45	0.45	0.50	0.50	0.50	0.50	0.50	
UV blocker								2.12
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

Table 3

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	Example 15	**Example 16**	**Example 17**	**Example 1**	**Example 2**	**Comparative Example 1**	**Comparative Example 2**	**Example 3**	**Example 4**	**Example 5**	**Example 6**
Total Silicone (%)	48.82	48.82	48.82	49.04	50.35	48.80	50.80	50.80	48.78	52.78	48.63
Sum NVP+ VMA (%)	36.17	36.17	36.17	34.72	35.28	36.10	34.10	34.10	36.10	36.10	38.72
Sum HOB + IBM (%)	14.47	14.47	14.47	15.60	13.72	14.40	14.40	14.40	14.40	10.40	9.00
Sum Si-2 (Formula 2) + Si-3 + IBM + HOB (%)	23.51	23.51	23.51	37.67	26.31	23.40	25.40	30.40	25.40	21.40	27.48
Sum Si-2 (Formula 2) + Si-3 + VMA + NVP (%)	45.21	45.21	45.21	56.79	47.87	45.10	45.10	50.10	47.10	47.10	57.20
Ratio Si-1 (Si-1a):Si-2 (Formula 2)	81:19	81:19	81:19	55:45	75:25	82:18	78:22	69:31	77:23	79:21	63:37
Ratio NVP:VMA	75:25	75:25	75:25	70:30	30:70	75:25	79:21	79:21	75:25	75:25	0:1
Ratio HOB:IBM	63:37	63:37	63:37	88:12	88:12	63:37	63:37	63:37	76:24	87:13	77:23
Ratio (NVA+VMA):(Si-1 (Si-1a) + Si-2 + Si-3)	42.6:57.4	42.6:57.4	42.6:57.4	41.5:58.5	41.2:58.8	42.5:57.5	40.2:59.8	40.2:59.8	42.5:57.5	41.5:58.5	44.3:55.7
Ratio Si-2 (Formula 2):(HOB+IBM)	38:62	38:62	38:62	59:41	48:52	38:62	43:57	53:47	43:57	51:49	67:33

Table 4

	US8129442										
	Example 15	**Example 16**	**Example 17**	**Example 1**	**Example 2**	**Comparative Example 1**	**Comparative Example 2**	**Example 3**	**Example 4**	**Example 5**	**Example 6**
Diameter (mm)				14.23	14.22	14.4	14.26	14.3	14.47	14.44	14.20
Base Curve (mm)				8.63	8.67	8.72	8.61	8.76	8.79	8.75	8.60
EWC (%)	44	55	30	47	47	49	48	47	49	49	51
Young's Modulus (MPa)				0.76	0.91	0.71	0.74	0.68	0.74	0.85	0.64
Dk (barrers)	115	90	150	128	140		127	131	124	139	129
Tensile Strength (MPa)	3	3	2.8	0.61	0.63	1.02	1.3	0.85	0.85	0.86	0.54
Sessile Drop Contact Angle (degrees)	44	40	50	20	24	21.1			25.4	27.5	20.0

[00123] In Table 3, "(Formula 2)" refers to the general structure of the compound of Formula 2 in this description, and Si-2 is a specific embodiment within Formula 2.

[00124] It is surprising that the particular selection of selection of the formulation of the present invention can cause such a significant reduction in the tensile strength of the resulting lens. The lenses of the present invention retain the other advantageous features seen in prior art lenses formed using the same combination of siloxane monomers, such as high Dk and good sessile drop contact angle.

[00125] Although the disclosure herein refers to certain illustrated examples, it is to be understood that these examples are presented by way of example and not by way of limitation. The intent of the foregoing detailed description, although discussing exemplary examples, is to be construed to cover all modifications, alternatives, and equivalents of the examples as may fall within the spirit and scope of the invention as defined by the additional disclosure.

[00126] A number of publications and patents have been cited hereinabove. Each of the cited publications and patents are hereby incorporated by reference in their entireties.

Claims

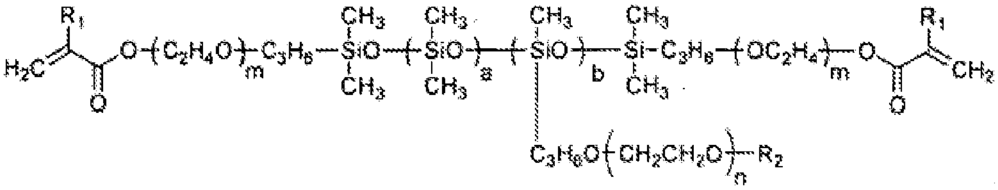
1. A silicone hydrogel contact lens formulation, comprising:

(i) a silicone component; and

(ii) a silicone-free component, wherein

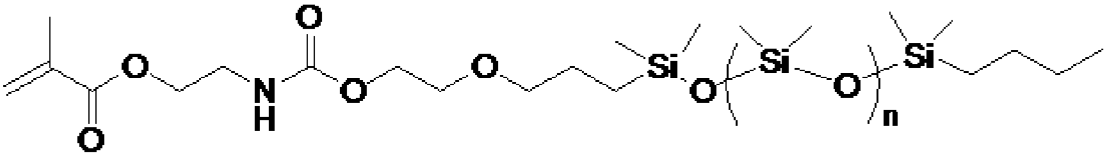
the silicone component comprises:

(a) a compound of Formula 1



wherein R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a C_{1-4} hydrocarbon group; m represents an integer of from 0 to 10; n represents an integer of from 4 to 100; a and b represent integers of 1 or more; a+b is from 20 to 500; b/(a+b) is from 0.01 to 0.22, and the configuration of siloxane units includes a random configuration; and

(b) a compound of Formula 2



wherein n is 10 to 25, and the compound of Formula 1 and the compound of Formula 2 are present in the formulation at a weight ratio from 50:50 to 80:20; and

the silicone-free component comprises an N-vinyl amide component (c); and a methacrylate component (d), wherein

the N-vinyl amide component (c) comprises N-vinyl N-methyl acetamide (VMA); and

the methacrylate component (d) comprises hydroxybutyl methacrylate (HOB) and isobornyl methacrylate (IBM), wherein the hydroxybutyl methacrylate and isobornyl methacrylate are present in the formulation at a weight ratio from 60:40 to 90:10,

wherein if the total amount of IBM in the contact lens formulation is greater than 5 weight percent, one or more of:

(i) the weight ratio of the compound of Formula 1 to the compound of Formula 2 is from 50:50 to 75:25, preferably from 65:35 to 70:30;
(ii) the compound of Formula 2 is present in an amount of at least 12 weight percent;
(iii) the compound of Formula 1 is present in an amount of less than 38 weight percent;

(iv) the weight ratio of the compound of Formula 2 to the total of the methacrylate component is greater than 0.9:1;

(v) the weight ratio of compound of Formula 1 to the compound of Formula 2 is less than 3:1; and

(vi) the total amount of mono(meth)acrylate compounds in the composition is greater than 26 weight percent.

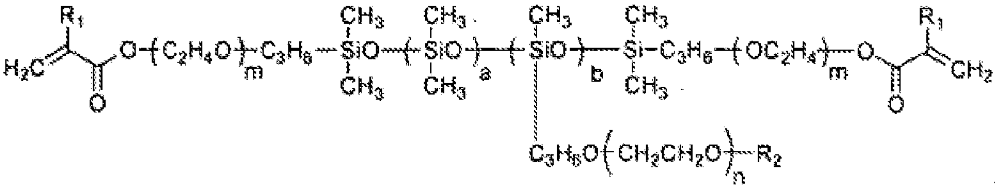
2. A silicone hydrogel contact lens formulation, comprising:

(i) a silicone component; and

(ii) a silicone-free component, wherein

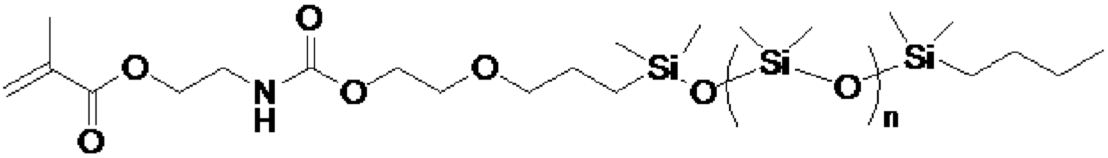
the silicone component comprises:

(a) a compound of Formula 1



wherein R_1 is selected from either hydrogen or a methyl group; R_2 is selected from either hydrogen or a $C_{1\text{-}4}$ hydrocarbon group; m represents an integer of from 0 to 10; n represents an integer of from 4 to 100; a and b represent integers of 1 or more; a+b is from 20 to 500; b/(a+b) is from 0.01 to 0.22, and the configuration of siloxane units includes a random configuration; and

(b) a compound of Formula 2



wherein n is an integer from 10 to 25, and the compound of Formula 1 and the compound of Formula 2 are present in the formulation at a weight ratio from 50:50 to 80:20; and

the silicone-free component comprises:

(c) an N-vinyl amide component; and

(d) a methacrylate component, wherein

the N-vinyl amide component (c) comprises N-vinyl N-methyl acetamide (VMA); and

the methacrylate component (d) comprises hydroxybutyl methacrylate (HOB) and isobornyl methacrylate (IBM), wherein the hydroxybutyl methacrylate and isobornyl methacrylate are present in the formulation at a weight ratio from 60:40 to 90:10, wherein if the hydroxybutyl methacrylate to isobornyl methacrylate weight ratio is 60:40 to 65:35, one or more of:

(i) the weight ratio of the compound of Formula 1 to the compound of Formula 2 is from 50:50 to 75:25, preferably from 65:35 to 70:30;
(ii) the compound of Formula 2 is present in an amount of at least 12 weight percent;
(iii) the compound of Formula 1 is present in an amount of less than 38 weight percent;
(iv) the weight ratio of the compound of Formula 2 to the total of the methacrylate component is greater than 0.9:1;
(v) the weight ratio of compound of Formula 1 to the compound of Formula 2 is less than 3:1; and
(vi) the total amount of mono(meth)acrylate compounds in the composition is greater than 26 weight percent.

3. The formulation of claim 1 or claim 2, further comprising a photoinitiator, a thermal initiator, a crosslinking monomer, a UV blocker, and a tinting agent.

4. The formulation of any one of the preceding claims, wherein the N-vinyl amide component (c) comprises VMA and N-vinyl pyrrolidone (NVP).

5. The formulation of claim 4, wherein the ratio of NVP to VMA is about 70:30 or about 30:70.

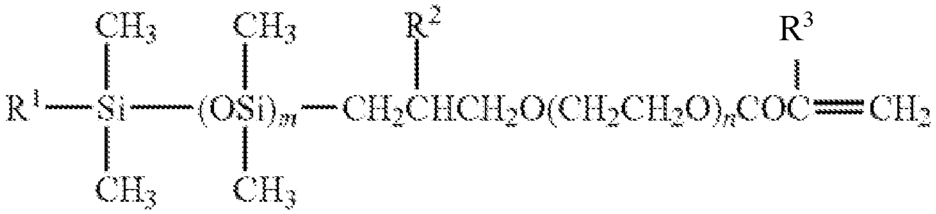
6. The formulation of any preceding claim wherein the weight ratio of the compound of Formula 1 to the compound of Formula 2 is 50:50 to 77:23.

7. The formulation of claim 4, wherein the weight ratio of NVP to VMA is 70:30 to 30:70.

8. The formulation of claim 4 or claim 5, wherein the weight ratio of HOB to IBM is from 85:15 to 90:10, and preferably about 88:12.

9. The formulation of claim 1, wherein:
the ratio of Formula 1 to Formula 2 is from 53:47 to 57:43;
the N-vinyl amide component consists essentially of NVP and VMA, wherein the ratio of NVP:VMA is from 68:32 to 72:28; and
the methacrylate component consists essentially of HOB and IBM, wherein the ratio of HOB to IBM is from 85:15 to 90:10.

10. The formulation of claim 1, wherein:
the silicone component consists essentially of Formula 1, Formula 2 and Formula 3:



$$R^1-\overset{CH_3}{\underset{CH_3}{Si}}-(O\overset{CH_3}{\underset{CH_3}{Si}})_m-CH_2\overset{R^2}{C}HCH_2O(CH_2CH_2O)_nCO\overset{R^3}{C}=CH_2$$

wherein m represents an integer of from 3 to 12, n represents an integer from 1 to 10, R^1 is selected from an alkyl group having from 1 to 4 carbon atoms, and each of R^2 and R^3 of Formula 3 is independently selected from a hydrogen atom or a methyl group, wherein Formula

3 is present in an amount of less than 0.6 weight percent of the formulation;
wherein the ratio of Formula 1 to Formula 2 is from 60:40 to 65:35;
the N-vinyl amide component consists essentially of VMA; and
the methacrylate component consists essentially of HOB and IBM, wherein the ratio of HOB to IBM is from 75:25 to 80:20.

11. A silicone hydrogel contact lens comprising the polymerized reaction product of the formulation of any preceding claim.

12. The silicone hydrogel contact lens of claim 11, which has a tensile strength of from 0.4 MPa to 1 MPa.

13. The silicone hydrogel contact lens of claim 11 or claim 12, which has a sessile drop contact angle less than 30 degrees.

14. The silicone hydrogel contact lens of any one of claims 11-13, which has an equilibrium water content from 45 weight % to 55 weight %.

15. The silicone hydrogel contact lens of any one of claims 11-14, which has an oxygen permeability from 110-140 barrers.

16. The silicone hydrogel contact lens of any one of claims 11-15, which has a Young's modulus from 0.3 MPa to 1.1 MPa.

17. The silicone hydrogel contact lens of any one of claims 11-16, which has a chord diameter from 13.5 to 15.5 mm and a base curve from 7.5 to 9.5 mm.

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Application No:	GB2311166.9	**Examiner:**	Mr Jason Scott
Claims searched:	1-17	**Date of search:**	20 September 2023

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US 2013/0176530 A1 (GOODENOUGH et al.)
A	-	US 2014/0009735 A1 (ZHENG et al.)
A	-	US 2012/0220688 A1 (WANG et al.)
A	-	WO 2011/041523 A2 (COOPERVISION INT HOLDING CO LP)

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

The following online and other databases have been used in the preparation of this search report

CAS ONLINE, SEARCH PATENT

International Classification:

Subclass	Subgroup	Valid From
G02B	0001/04	01/01/2006
C08F	0030/08	01/01/2006
C08F	0220/18	01/01/2006
C08F	0220/20	01/01/2006
C08F	0220/28	01/01/2006
C08F	0220/30	01/01/2006
C08F	0226/02	01/01/2006
C08G	0077/442	01/01/2006
C08L	0033/10	01/01/2006
C08L	0083/04	01/01/2006
G02C	0007/04	01/01/2006