



(51) International Patent Classification:

C08G 77/42 (2006.01) *C08F* 290/14 (2006.01)
C08F 283/12 (2006.01) *C08L* 83/10 (2006.01)

(21) International Application Number:

PCT/US2014/025878

(22) International Filing Date:

13 March 2014 (13.03.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/783,762 14 March 2013 (14.03.2013) US

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



(54) Title: HYDROPHILIC SILICONE POLYMERS

(57) Abstract: A method of preparing a hydrophilic hybrid silicone polymer includes combining (a) a silicone having one or more reactive or polymerizable groups and (b) at least one hydrophilic monomer in the presence of (c) at least one initiator to form a mixture. The method further includes polymerizing the mixture to form the hydrophilic hybrid silicone polymer.

HYDROPHILIC SILICONE POLYMERS

FIELD OF THE INVENTION

[0001] The present invention relates to novel hydrophilic silicone polymers and methods of their preparation. The hydrophilic silicone materials can be used, for example, in medical applications.

SUMMARY OF THE INVENTION

[0002] According to one process, a method of preparing a hydrophilic hybrid silicone polymer includes combining (a) a silicone having one or more reactive or polymerizable groups and (b) at least one hydrophilic monomer in the presence of (c) at least one initiator to form a mixture. The method further includes polymerizing the mixture to form the hydrophilic hybrid silicone polymer.

[0003] According to another process, a method of forming a hydrophilic silicone elastomer includes combining silicone and at least one hydrophilic monomer in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups. The method further includes further reacting the hydrophilic hybrid silicone polymer with one or more reactive groups to form the hydrophilic silicone elastomer.

[0004] According to yet another process, a method of forming a hydrophilic silicone elastomer includes combining silicone and at least one hydrophilic monomer in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups. The method further includes dispersing the hydrophilic hybrid silicone polymer into a silicone matrix, the silicone matrix being formed by reacting silicone with unsaturated hydrocarbon functional groups with silicone hydride groups in the presence of a hydrolisation catalyst.

[0005] According to one embodiment, a hydrophilic hybrid silicone polymer liquid includes at least one silicone polymerized with at least one hydrophilic monomer. The at least one hydrophilic monomer includes diallyldimethyl ammonium chloride, other quaternary salts, acrylamide derivatives, or a combination thereof.

[0006] Additional aspects of the invention will be apparent to those of ordinary skill in the art in view of the detailed description of various embodiments, a brief description of which is provided below.

DETAILED DESCRIPTION

[0007] All amounts, ratios, and percentages are by weight unless otherwise indicated. The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of specification. The disclosure of ranges includes the range itself

and also anything subsumed therein, as well as endpoints. Similarly, the disclosure of Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, the Markush group including a hydrogen atom, an alkyl group, an aryl group, or an aralkyl group includes the member alkyl individually; the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0008] The invention described in the embodiments herein relates to hydrophilic silicone polymers (liquids and solids/elastomers) and methods of making the same. The hydrophilic silicone polymers of the embodiments discussed herein have one or more improved properties over those of known compositions and can generally be prepared at a moderate cost.

[0009] Silicone gels, rubbers, and elastomers are the terms generally used to describe elastic materials prepared by the crosslinking of polyorganosiloxanes. Gels, elastomers, and rubbers are differentiated by the extent of crosslinking within the siloxane network, by hardness, and elasticity. These materials may be used in medical wound dressings to treat most types of wounds safely. Since silicone is inert, biocompatible, and has good gas permeability, it does not interact chemically with the wound or have any substantial effect upon the cells responsible for the healing process. However, its hydrophobic property may result in poor wettability by body liquids and an uncomfortable feeling on the skin. Thus, dressings with hydrophilic silicone components promote wound healing by providing a moist environment, while removing excess exudate and toxic components, and further serve as a barrier to protect the wound from secondary bacterial infection.

[0010] Generally speaking, the term "hydrophilic" refers to a material that it is wettable by an aqueous medium. Hydrophilic silicone materials used as wound dressings for application to living tissues are desired to maintain a moist wound healing environment, be breathable (permeable) for moisture, promote wound exudate absorption to prevent maceration, and also enhance transportation of wound exudate through and into the bulk silicone layer or material.

[0011] The methods of the embodiments discussed herein generally include two parts: (1) preparation of hydrophilic hybrid silicone polymers by polymerization of hydrophilic monomer(s) with silicone including unsaturated hydrocarbon functional groups (e.g., vinyl, allyl, acrylate, or alkylacrylate) in the presence of one or more initiators; and (2) formation of a hydrophilic silicone gel or elastomer. These processes will generally be referred to as "Part 1" and "Part 2," respectively, below. The hydrophilic silicone hybrid polymer is generally uniform and stable in a liquid form such that it does not visibly separate after three days at room temperature. The hydrophilic silicone hybrid polymer, which may be in the form of liquid, gel, solid, flake, or powder, may be solidified into a hydrophilic silicone gel or elastomer by further reaction or by dispersion into a silicone matrix. This final hydrophilic

silicone product may be in the form of gel, solid, or porous foam with open cells or closed cells.

[0012] Since hydrophilic silicone hybrid polymers of the embodiments described herein have a generally uniform microstructure from the reaction or polymerization of a hydrophilic monomer with silicone, gels or elastomers formed using those hydrophilic silicone hybrid polymers may be endowed with high water absorption and/or water permeation (diffusion rates) through their layers/films and maintain desirable characteristics typically associated with silicone, such as good biocompatibility and creation of a soft and comfortable feeling on the skin. Furthermore, many of the hydrophilic silicone polymers described herein are antimicrobial by virtue of the introduction of an antimicrobial hydrophilic monomer into the silicone network by polymerization.

[0013] According to one embodiment, the hydrophilic silicone gel/elastomer may be prepared by combining a hydrophilic hybrid silicone with one or more reactive groups (e.g., unsaturated groups including vinyl, allyl, acrylate, silanol (SiOH)) and one or more other reactive materials through their reactions. The one or more other reactive materials can be reacted with the one or more reactive groups in the hydrophilic hybrid silicone material. The reaction may, for example, be between silicone-hydride (SiH) and a vinyl/allyl group, mercapto (SH) and an acrylate, alkoxy (Si(OR)) and a SiOH group, acetoxysilane (Si(OOCCH₃)) and a SiOH group, enoxy (CH₃C(=CH₂)O-Si) and a SiOH group, oxime (CH₃C₂H₅C=NO-Si) and a SiOH group, or amine ((CH₃)₂N-Si) and a SiOH group.

[0014] In another embodiment, the hydrophilic silicone gel/elastomer may be prepared by the combination of a hydrophilic hybrid silicone polymer with reactive groups such as, but not limited to, one or more unsaturated groups including vinyl, allyl, acrylate, or alkylacrylate, and solidification. The components may be combined through physicochemical methods such as, for example, light, UV exposure, heating/cooling, radiation, moisture, ozone, high pressure, low pressure, magnetic fields, electric fields, combinations thereof, or the like. According to another embodiment, a hydrophilic silicone solid/elastomer may be prepared by dispersion of the hydrophilic hybrid silicone polymer with or without any reactive groups into a silicone matrix such as, but not limited to, one or more unsaturated groups including vinyl, allyl, acrylate, and silanol (SiOH).

SILICONE FOR HYDROPHILIC HYBRID SILICONE POLYMERS – PREPARATION BY REACTION (Part 1)

[0015] The silicone used for preparation of hydrophilic hybrid silicone materials of the embodiments described herein may, for example, be selected from any types of silicone including M, D, T, Q structures into molecular compositions that are known in the art. In some embodiments, the silicone that is used in this preparation includes a liquid silicone. The silicone formulation may include siloxy units having the formula (RR¹R²SiO_{1/2}),

($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), and/or ($SiO_{4/2}$), where at least one of R, R^1 , R^2 is a reactive or polymerizable group including, but not limited to, unsaturated hydrocarbon functional groups such as vinyl, allyl, acrylate functional groups such as acryloxyalkyl groups, or methacrylate functional groups such as methacryloxyalkyl groups or acrylamide. The other non-polymerizable groups among the R, R^1 , R^2 may be independently selected from monovalent organic groups. These units may be alternatively described as organopolysiloxane segments and are known in the art as M, D, T, and Q units, respectively. In one embodiment, the silicone compositions include "M" siloxy units. In another embodiment, the silicone compositions include "D" siloxy units. In still another embodiment, the silicone compositions include "T" siloxy units. In a further embodiment, the silicone compositions include "Q" siloxy units. In even further embodiments, the silicone compositions include "M" and "D" units, "M" and "T" units, "M" and "Q" units, "D" and "T" units, "D" and "Q" units, or "T" and "Q" units.

[0016] In the formulae above, the monovalent group of R, R^1 , R^2 is independently a hydrocarbon or halogenated hydrocarbon group including 1 to 30 carbon atoms. Non-limiting examples include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, and octadecyl groups, and an aliphatically unsaturated group such as an alkenyl group. Suitable alkenyl groups include from 2 carbon to about 6 carbon atoms and may be, but are not limited to, vinyl, allyl, and hexenyl, cycloalkyl groups such as cyclohexyl, aryl groups (e.g., phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl), and halogenated hydrocarbon groups (e.g., 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl groups). The number of siloxy units may vary. The number and type of siloxy units may affect the molecular weight of the organopolysiloxane segment and, hence, the molecular weight of the composition.

[0017] In the formulae above, the monovalent R, R^1 , R^2 groups may also include, but are not limited to, cyanofunctional groups, monovalent hydrocarbon groups, and combinations thereof. The monovalent hydrocarbon groups may include alkyl groups (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, s-butyl, t-butyl, pentyl, neopentyl, octyl, undecyl, and octadecyl groups), cycloalkyl groups such as cyclohexyl groups, aryl groups (e.g., phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl groups), halogenated hydrocarbon groups (e.g., 3,3,3-trifluoropropyl, 3-chloropropyl, dichlorophenyl, and 6,6,6,5,5,4,4,3,3-nonafluorohexyl groups), and combinations thereof. The cyano-functional groups may include cyanoalkyl groups such as cyanoethyl groups, cyanopropyl groups, and combinations thereof.

[0018] In the formulae above, the monovalent R, R^1 , R^2 groups may also include alkyloxypoly(oxyalkylene) groups such as propyloxy(polyoxyethylene), propyloxypoly(oxypropylene) and propyloxy-poly(oxypropylene)-co-poly(oxyethylene) groups, halogen substituted alkyloxypoly(oxyalkylene) groups such as

perfluoropropoxy(polyoxyethylene), perfluoropropoxypoly(oxypropylene) and perfluoropropoxy-poly(oxypropylene) copoly(oxyethylene) groups, alkenyloxypoly(oxyalkylene) groups such as allyloxypoly(oxyethylene), allyloxypoly(oxypropylene) and allyloxy-poly(oxypropylene) copoly(oxyethylene) groups, alkoxy groups such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and ethylhexyloxy groups, aminoalkyl groups such as 3-aminopropyl, 6-aminoethyl, 11-aminoundecyl, 3-(N-allylamino)propyl, N-(2-aminoethyl)-3-aminopropyl, N-(2-aminoethyl)-3-aminoisobutyl, *p*-aminophenyl, 2-ethylpyridine, and 3-propylpyrrole groups, hindered aminoalkyl groups such as tetramethylpiperidinyl oxypropyl groups, epoxyalkyl groups such as 3-glycidoxypropyl, 2-(3,4-epoxycyclohexyl)ethyl, and 5,6-epoxyhexyl groups, ester functional groups such as acetoxymethyl and benzoyloxypropyl groups, hydroxyl functional groups such as hydroxy and 2-hydroxyethyl groups, isocyanate and masked isocyanate functional groups such as 3-isocyanatopropyl, tris-3-propylisocyanurate, propyl-t-butylcarbamate, and propylethylcarbamate groups, aldehyde functional groups such as undecanal and butyraldehyde groups, anhydride functional groups such as 3-propyl succinic anhydride and 3-propyl maleic anhydride groups, carbonyl and carboxy functional groups such as 3-carboxypropyl, 2-carboxyethyl, and 10-carboxydecyl groups, functional groups of carboxalkoxy, carboxamido, amidino, nitro, cyano, primary amino, secondary amino, acylamino, alkylthio, sulfoxide, sulfone, metal salts of carboxylic acids such as zinc, sodium, and potassium salts of 3-carboxypropyl and 2-carboxyethyl groups, and any combination thereof. Any metal atoms may be included into the R groups and/or the siloxane chains.

HYDROPHILIC MONOMER FOR HYDROPHILIC HYBRID SILICONE POLYMER PREPARATION BY REACTION (Part 1)

[0019] The hydrophilic monomer used to form the hydrophilic hybrid silicone polymer of the embodiments described herein may include, but is not limited to, the molecules containing vinyl, allyl, acrylates or alkylacrylates and hydroxyl, poly(ethylene glycol), ether, cyano, carboxyl groups, for example, 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), 3-hydroxypropyl methacrylate (HPMA), (3-acryloyloxy)-2-hydroxypropyl methacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(ethylene glycol) dimethacrylate, 2-cyanoethyl acrylate, β -carboxyethyl acrylate vinyl ethyl ether, vinyl phenyl ether, diallyl maleate, or any combination thereof.

[0020] The hydrophilic monomer used to form the hydrophilic hybrid silicone polymer of the embodiments described herein may include, but is not limited to, anionic polymerizable monomers of anhydride such as maleic anhydride, acid (e.g., carboxylic acid, phosphoric acid, sulfuric acid) or metal or non-metal salts (e.g., carboxylate, phosphate, sulfate) including one or more groups of vinyl, allyl, acrylates, and alkylacrylates in their

molecules, for example, acrylic acid, sodium methacrylate, and sodium 1-allyloxy-2-hydroxypropyl sulfonate

[0021] The hydrophilic monomer used to form the hydrophilic silicone gel/elastomer described in the embodiments herein may include, but is not limited to, cationic polymerizable monomers of quaternary ammonium salts such as, for example, (1) one or more groups of allyl- or vinyl-containing quaternary ammonium salts such as diallyldimethyl ammonium chloride, (2) one or more groups of acrylates, methacrylates, or other alkylacrylates including quaternary ammonium, for example, methacryloxyethyl alkyl (or aryl) ammonium chloride, methacryloxyethyl alkyl (or aryl) ammonium bromide, where alkyl is C_nH_{2n+1} ($n=1-18$), the quaternary ammonium salt of 1-methacryloyl-4-methylpiperazine, *N,N*-diallyl-*N*-carboethoxymethyl-*N*-carbomethoxypentylammonium chloride, (3) amide with one or more acryl groups and its derivatives, for example, the quaternized salts of methacrylamide-3-(aminomethyl)pyridine, or any combination thereof.

[0022] In some embodiments, the quaternary ammonium monomers are hydrophilic and antimicrobial. Their introduction into silicone gels and elastomers endow these silicones with good performance and allow their use in transdermal drug delivery and wound management applications to secure patches or wound dressings to the skin with minimum impact on the contacting area.

INITIATOR AND CATALYST FOR HYDROPHILIC HYBRID SILICONE POLYMER PREPARATION BY REACTION (Part 1)

[0023] The initiator used to prepare the hydrophilic hybrid silicone polymers described herein may be a catalyst that can initiate polymerization and/or copolymerization of the hydrophilic monomer, the silicone, or both the silicone and the hydrophilic monomer. The catalyst may be a free radical initiator, for example, azo-compounds, peroxides persulfate, disulfides, metal complexes that are decomposed to radicals by heat, light, or a redox process, any combination thereof, or the like. For example, the peroxide may be benzyl peroxide (BPO), diacryl peroxide (LPO), di-tert-butyl peroxyoxalates (DBPOX). Suitable azo-compounds may include, but are not limited to, azobisisobutyronitrile (AIBN) and di-tert butyl hyponitrite (DTBN). In another embodiment, the catalyst is a condensation catalyst including, but not limited to, a tin compound, alkaline metal (Li, Na, K, Rb, Cs) compound, alkaline earth metal (Mg, Ca, Ba, Sr) compound, or an amine such as tertiary amine or secondary amine. In another embodiment, the initiator includes a photoinitiator such as, but not limited to, acetophenone such as 1-hydroxycyclohexyl phenyl ketone or 2,2-diethoxyacetophenone, benzil/benzoin compounds such as 4,4'-dimethylbenzil or benzoin methyl ether, benzophenone such as 4-hydroxybenzophenone, 4-benzoylbiphenyl, or 4-(dimethylamino)benzophenone, thioxanthenes such as thioxanthen-9-one or 10-methylphenothiazine, cationic photoinitiators such as boc-methoxyphenyldiphenylsulfonium

triflate, (4-bromophenyl)diphenylsulfonium triflate, diphenyliodonium nitrate, (4-phenylthiophenyl)diphenylsulfonium triflate, and others such as 2-tert-butylantraquinone, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide .

[0024] It is contemplated that any suitable amount of initiator or catalyst may be used as long as there is a sufficient amount of initiator or catalyst to accelerate a reaction between the unsaturated hydrocarbon group into the silicone and the hydrophilic monomer in the reaction mixture at room temperature or at temperatures above room temperature. The exact amount of catalyst generally depends on the particular catalyst utilized. In some embodiments, the catalyst is added in an amount from about 0.001 to about 5 weight parts per one hundred parts of the reaction mixture composed of the silicone, hydrophilic monomers, and the optional components such as water, solvents, surfactant, and other additives. In other embodiments, the catalyst is added in an amount from about 0.05 to about 0.5 weight parts per one hundred parts of the reaction mixture.

PREPARATION OF HYDROPHILIC HYBRID SILICONE POLYMERS (Part 1)

[0025] A hydrophilic hybrid silicone polymer liquid according to one embodiment includes: (a) a silicone having one or more reactive or polymerizable groups; and (b) at least one hydrophilic monomer. The hydrophilic hybrid silicone polymer is polymerized in the presence of (c) at least one initiator. The resulting hydrophilic hybrid silicone polymer does not visibly separate after three days at room temperature and is, thus, considered stable.

[0026] The preparation of a hydrophilic hybrid silicone polymer by combining at least one hydrophilic monomer with a silicone can be conducted neat or in the presence of water or a solvent. The solvent may include, but is not limited to, an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone, an aromatic hydrocarbon such as benzene, toluene, or xylene, an aliphatic hydrocarbon such as heptane, hexane, or octane, an ether such as dimethyl ether or tetrahydrofuran (THF), a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl acetonitrile, tetrahydrofuran, white spirits, mineral spirits, naphtha, any combination thereof, or the like.

[0027] The amount of water or solvent can be up to 95 weight percent. In another embodiment, the amount of water or solvent is about 10 to about 50 weight percent. The weight percent is based on the total weight of components in the reaction mixture. The solvent and/or other volatile materials used during the reaction may be subsequently removed from the resulting hydrophilic hybrid silicone polymer using any suitable method.

[0028] Additional components, including as additives known to enhance the targeting reactions and/or to stop or prohibit the side reactions, may also be added to the reaction.

These components include may include thermal stabilizer during the reaction and chain transfer agents, inhibitors, and retarders after the reaction is completed.

[0029] The polymerization and reaction of and between the hydrophilic monomers and the reactive silicones may be realized in many ways in the presence of the initiator, including, but not limited to, in bulk (e.g., both compatible), a solution (e.g., both soluble into a common solvent or a solvent mixture), in a dispersion, in an emulsion, or the like. By emulsion polymerization, the monomer may, optionally, be placed into an aqueous solution. The aqueous solution may include water and/or other solvent(s). The liquid mixture of monomer, silicone and water, and initiator may then be initiated for polymerization by heat, light, radiation, or the like in the presence of or in the absence of one or more surfactants and/or other additives. Water, other solvent(s), and/or other volatile material(s) used in the reaction may be removed after the polymerization. In reactions conducted in the presence of a free radical initiator, peroxide, and/or an azo-compound, a purge of one or more inert gases (e.g., nitrogen or helium) for over 10 minute may be required or desirable to remove the oxygen from the reaction system so that the polymerization may be initiated and not be inhibited by oxygen.

[0030] The above-described hydrophilic hybrid silicone polymer used to form the hydrophilic silicone polymer liquid and/or solid/elastomer may include copolymers, a mixture of homopolymers, or a combination of copolymers and homopolymers of the silicone and the hydrophilic monomer. The hydrophilic hybrid silicone polymer may or may not include reactive functional groups. The hydrophilic hybrid silicone polymer may be liquid, gel, solid powder, solid flakes, or elastomer. In one embodiment, the hydrophilic hybrid silicone polymer is a liquid or a solid powder such that it may easily disperse into a silicone matrix and/or be easily processed to form a film or coating.

FORMATION OF HYDROPHILIC SILICONE GEL/ELASTOMERS (Part 2)

[0031] In one embodiment, a hydrophilic silicone gel/elastomer may be formed by combining the above-described hydrophilic hybrid silicone polymers with one or more reactive groups and (a) cured into a solid/elastomer by reaction with one or more other reactive materials, or (b) solidifying through physicochemical methods such as light, UV exposure, heating/cooling, radiation, moisture, ozone, high pressure, low pressure, magnetic fields, electric fields, combinations thereof, or the like. For example, a hydrophilic hybrid silicone polymer with unsaturated hydrocarbon functional groups such as vinyl, allyl or acrylate may be cured into a gel or elastomer by heat, light, and/or radiation in the presence or in the absence of peroxide(s). In another example, a hydrophilic hybrid silicone polymer with unsaturated hydrocarbon functional groups such as vinyl or allyl groups may be cured into a gel or elastomer by reaction with another silicone having one or more silicon hydride (SiH) groups in its molecules in the presence of a hydrosilation catalyst. The silicone with

one or more silicon hydride (SiH) groups used herein may follow the silicone with silicon hydride (SiH) groups for formation of the silicone matrix, as described below.

[0032] In another embodiment, a hydrophilic silicone solid/elastomer may be prepared by dispersion of the above hydrophilic hybrid silicone with or without any reactive groups into a silicone matrix. The silicone matrix may be formed from hydrosilation of silicone with unsaturated hydrocarbon functional groups and another silicone with silicon hydride (SiH) groups in the presence of a catalyst.

[0033] In one embodiment, a hydrophilic silicone elastomer includes a hydrophilic hybrid silicone polymer reacted with one or more reactive groups to form the hydrophilic silicone elastomer. The hydrophilic hybrid silicone polymer includes (a) silicone and (b) at least one hydrophilic monomer, wherein the silicone and the at least one hydrophilic monomer were combined in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups.

[0034] In another embodiment, a hydrophilic silicone elastomer includes a hydrophilic hybrid silicone polymer dispersed into a silicone matrix. The hydrophilic hybrid silicone polymer includes (a) silicone and (b) at least one hydrophilic monomer, wherein the silicone and the at least one hydrophilic monomer were combined in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups. The hydrophilic silicone matrix may be formed by reacting silicone with unsaturated hydrocarbon functional groups with silicone hydride groups in the presence of a hydrolisation catalyst.

[0035] Silicone formulations useful in preparing the hydrophilic silicone gel/elastomer with the dispersed hydrophilic hybrid silicone polymer described herein generally include one or more functional groups configured to react with one another and/or may be polymerized to form longer chains and/or cross-linked networks.

[0036] The silicone formulation of the embodiments described herein may, for example, be selected from any types of silicone including M, D, T, Q structures into molecular compositions that are known in the art. In some embodiments, the silicone formulation that is used in the methods described herein is a liquid silicone. The silicone formulation may include siloxy units having the formula $(RR^1R^2SiO_{1/2})$, $(R^1R^2SiO_{2/2})$, $(RSiO_{3/2})$, and/or $(SiO_{4/2})$, where R, R^1 , R^2 may be independently selected from a hydrogen atom and a monovalent organic group. These units may be alternatively described as organopolysiloxane segments and are known in the art as M, D, T, and Q units, respectively. In one embodiment, the silicone compositions include "M" siloxy units. In another embodiment, the silicone compositions include "D" siloxy units. In still another embodiment, the silicone compositions include "T" siloxy units. In a further embodiment, the silicone compositions include "Q" siloxy units. In even further embodiments, the silicone

compositions include "M" and "D" units, "M" and "T" units, "M" and "Q" units, "D" and "T" units, "D" and "Q" units, or "T" and "Q" units.

[0037] The organopolysiloxane units in the silicone components may further include a cyclic siloxane ring including n atoms of silicon with $n \geq 3$ (in one embodiment, $n = 3-6$) including $(R^1R^2SiO_{n/n})$, $(RHSiO_{n/n})$, $(R^1R^2SiO)_n$, $(RHSiO)_n$ units, or any combination thereof.

[0038] In the formulae above, the monovalent group of R , R^1 , R^2 is independently a hydrocarbon or halogenated hydrocarbon group including 1 to 30 carbon atoms. Non-limiting examples include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, and octadecyl groups or an aliphatically unsaturated group such as an alkenyl group. Suitable alkenyl groups contain from 2 carbon to about 6 carbon atoms and may be, but are not limited to, vinyl, allyl, and hexenyl, cycloalkyl groups such as cyclohexyl, aryl groups such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl, and halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl groups. The number of siloxy units may vary. The number and type of siloxy units may affect the molecular weight of the organopolysiloxane segment, and hence the molecular weight of the composition.

[0039] The R , R^1 , R^2 groups may also include, but are not limited to, acrylate functional groups such as acryloxyalkyl groups, methacrylate functional groups such as methacryloxyalkyl groups, cyanofunctional groups, monovalent hydrocarbon groups, and any combination thereof. The monovalent hydrocarbon groups may include alkyl groups such as methyl, ethyl, propyl, isopropyl, n-butyl, s-butyl, t-butyl, pentyl, neopentyl, octyl, undecyl, and octadecyl groups, cycloalkyl groups such as cyclohexyl groups, aryl groups such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl groups, halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, dichlorophenyl, and 6,6,6,5,5,4,4,3,3-nonafluorohexyl groups, and any combination thereof. The cyano-functional groups may include cyanoalkyl groups such as cyanoethyl and cyanopropyl groups and any combination thereof.

[0040] The R , R^1 , R^2 groups may also include alkyloxypoly(oxyalkylene) groups such as propyloxy(polyoxyethylene), propyloxypoly(oxypropylene) and propyloxy-poly(oxypropylene)-co-poly(oxyethylene) groups, halogen substituted alkyloxypoly(oxyalkylene) groups such as perfluoropropyloxy(polyoxyethylene), perfluoropropyloxypoly(oxypropylene) and perfluoropropyloxy-poly(oxypropylene) copoly(oxyethylene) groups, alkenyloxypoly(oxyalkylene) groups such as allyloxypoly(oxyethylene), allyloxypoly(oxypropylene) and allyloxy-poly(oxypropylene) copoly(oxyethylene) groups, alkoxy groups such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and ethylhexyloxy groups, aminoalkyl groups such as 3-aminopropyl, 6-aminoethyl, 11-aminoundecyl, 3-(N-allylamino)propyl, N-(2-aminoethyl)-3-aminopropyl, N-

(2-aminoethyl)-3-aminoisobutyl, *p*-aminophenyl, 2-ethylpyridine, and 3-propylpyrrole groups, hindered aminoalkyl groups such as tetramethylpiperidinyl oxypropyl groups, epoxyalkyl groups such as 3-glycidoxypropyl, 2-(3,4-epoxycyclohexyl)ethyl, and 5,6-epoxyhexyl groups, ester functional groups such as acetoxymethyl and benzoyloxypropyl groups, hydroxyl functional groups such as hydroxy and 2-hydroxyethyl groups, isocyanate and masked isocyanate functional groups such as 3-isocyanatopropyl, tris-3-propylisocyanurate, propyl-*t*-butylcarbamate, and propylethylcarbamate groups, aldehyde functional groups such as undecanal and butyraldehyde groups, anhydride functional groups such as 3-propyl succinic anhydride and 3-propyl maleic anhydride groups, carbonyl and carboxy functional groups such as 3-carboxypropyl, 2-carboxyethyl, and 10-carboxydecyl groups, functional groups of carboxalkoxy, carboxamido, amidino, nitro, cyano, primary amino, secondary amino, acylamino, alkylthio, sulfoxide, sulfone, metal salts of carboxylic acids such as zinc, sodium, and potassium salts of 3-carboxypropyl and 2-carboxyethyl groups, and combinations thereof. Any metal atoms may be included into the R groups and/or the siloxane chains.

[0041] The catalysts facilitating the hydrosilylation reaction may include, for example, any of the following or combinations thereof: chloroplatinic acid, alcohol-modified chloroplatinic acids, olefin complexes of chloroplatinic acid, complexes of chloroplatinic acid and divinyltetramethyldisiloxane, fine platinum particles adsorbed on carbon carriers, platinum supported on metal oxide carriers such as Pt(Al₂O₃), platinum black, platinum acetylacetonate, platinum(divinyltetramethyldisiloxane), platinum halides exemplified by PtCl₂, PtCl₄, Pt(CN)₂, complexes of platinum halides with unsaturated compounds exemplified by ethylene, propylene, and organovinylsiloxanes, styrenehexamethyldiplatinum, and RhCl₃(Bu₂S)₃.

[0042] Non-limiting examples of suitable liquid silicone formulations that are commercially available are DOW CORNING® 7-9800 SOFT SKIN ADHESIVE PART A, DOW CORNING® 7-9850 SOFT SKIN ADHESIVE PART A, and DOW CORNING® 7-9900 SOFT SKIN ADHESIVE PART A, organopolysiloxanes available from Dow Corning Corporation (Midland, MI). These liquid Part A compositions can be cured into gels or solids with their corresponding Part B compositions.

[0043] If desired, other components can be added to the silicone solid or elastomer composition including, but not limited to, fillers, pigments, low-temperature cure inhibitors, additives for improving adhesion, chain extenders, pharmaceutical agents, drugs, cosmetic agents, natural extracts, fluids or other materials conventionally used in gels, silicone fluids, silicone waxes, silicone polyethers, rheology modifiers such as thickening agents or thixotropic agents, any combination thereof, or the like. If filler is added, the filler may or may not react with the hydrophilic hybrid silicone polymers. The filler may be a liquid, a

solid, or a combination thereof. The filler may include polymer or small molecules in any form or shape, including solid particles, fibers, sheets, or plates.

ANTIMICROBIAL ADDITIVES

[0044] For the hydrophilic monomers without any antimicrobial activity used for preparation of hydrophilic hybrid silicone polymer, at least one antimicrobial additive may be added to the silicone liquid mixture prior to being cured into a gel or elastomer. The at least one antimicrobial additive may, for non-limiting example, include silver coated on E-powder, silver sulfate powder, silver sulfate powder coated on E-powder, silver nitrate coated on E-powder, silver nitrate powder, or any combination thereof.

[0045] E-powders, referenced above and in Table 1 below, refer to a family of silicone elastomeric particles produced by Dow Corning Toray Silicone Co., Ltd. Examples of suitable silicones that can be used herein include those described in U.S. Pat. Nos. 4,370,160, 4,742,142, 4,743,670, 5,387,624, 5,492,945, 5,945,471, 5,948,469, 5,969,039 and 7,393,582, which are hereby incorporated by reference in their entireties. These silicone elastomeric particles are prepared by various methods such as by curing liquid silicones into a wet emulsion or dispersion followed by drying, "in situ" particle formation by curing the liquid and forming into droplets, "in situ" particle formation during liquid spraying and then curing, etc.

[0046] In U.S. Pat. No. 4,370,160, microparticles, such as microspheres and microcapsules, comprising a solid organopolysiloxane are prepared by irradiating a dispersion of discrete entities with UV light. The discrete entities are dispersed in a UV-transparent fluid continuous phase and are sphere-like particles of a UV-curable, liquid organopolysiloxane composition, or such a liquid organopolysiloxane composition containing a material to be encapsulated. In U.S. Pat. No. 4,742,142, powdered, cured silicone rubber in the form of microfine particles is prepared by emulsifying a curable liquid silicone rubber composition in a mixture of water and a surfactant at a temperature of from 0 to 25°C, dispersing the curable composition in water heated to a temperature of at least 25°C and recovering the resultant cured particles. In U.S. Pat. No. 4,743,670, cured silicone rubber in the form of a finely divided powder is prepared by dispersing a heat-curable liquid silicone rubber composition in water maintained at a temperature of from 0 to 25°C, dispersing the resultant dispersion in a liquid heated to a temperature of at least 50°C, and recovering the resultant cured powder.

[0047] In U.S. Pat. No. 5,387,624, a powder mixture of cured silicone microparticles and inorganic microparticles is prepared by (i) forming a water-based suspension of a plurality of cured silicone microparticles having an average diameter of 0.1 to 200 micrometers, a plurality of inorganic microparticles having an average particle diameter of

0.1 to 200 micrometers and, optionally, at least one surfactant; and (ii) removing the water from the water-based suspension.

[0048] In U.S. Pat. No. 5,492,945, a cured silicone rubber composition is prepared by (i) preparing a water-based dispersion of a cured silicone powder having an average particle diameter of 0.1 to 200 micrometers and an amorphous silica micropowder that has an average particle diameter not exceeding 1 micrometer and a surface silanol group density of at least 2 silanol groups per 100 square angstroms; (ii) heating the water-based dispersion; and (iii) removing the water from the dispersion. The silica micropowder is immobilized on the surface of the cured silicone powder. In U.S. Pat. No. 5,945,471, a composite powder composition having excellent flowability and water repellency is disclosed, the composition comprising: (A) 100 parts by weight of a cured silicone powder that has an average particle size of 0.1 to 500 micrometers and contains 0.5 to 80 weight percent of a non-crosslinking oil; and (B) 0.1 to 100 parts by weight of a microfine inorganic powder, the inorganic powder being coated on the surface of the cured silicone powder. In U.S. Pat. No. 5,948,469, silicone rubber particulates coated with metal oxide microparticles are prepared, wherein the metal oxide microparticles are derived from a sol. The prepared silicone rubber particulates reduce aggregation of the particulate mass.

[0049] In U.S. Pat. No. 5,969,039, cured silicone powder having a uniform particle size is prepared, in which a platinum-alkenylsiloxane complex catalyst is added to a water-based dispersion of a silicone composition. The silicone composition is an organopolysiloxane having at least two silicon-bonded alkenyl groups in each molecule and an organopolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule. The catalyst is added and dispersed in the form of liquid particles with an average particle size in volumetric particle size distribution in water of no more than one micron. In U.S. Pat. No. 7,393,582, composite silicone rubber particles include silicone rubber particles A and silicone rubber particles B, wherein the surface of the particles A is covered with the particles B having sizes smaller than sizes of particles A.

[0050] Non-limiting examples of suitable silicone particles that are commercially available include DOW CORNING® Trefil E-500, DOW CORNING® Trefil E-506C, DOW CORNING® Trefil E-506S, DOW CORNING® Trefil E-506W, DOW CORNING® Trefil E-507, DOW CORNING® Trefil E-508, DOW CORNING® Trefil E-521, DOW CORNING® Trefil E-600, DOW CORNING® Trefil E-601, DOW CORNING® Trefil E-606, DOW CORNING® Trefil E-71, and DOW CORNING® 9506 POWDER, available from Dow Corning Corporation.

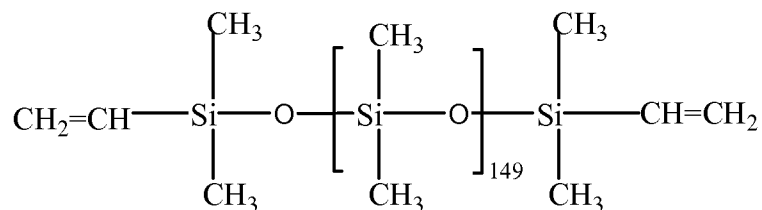
[0051] In some embodiments, the silver-loaded microparticles and silver-loaded nanoparticles can be dispersed into the formulation of the one or more polymers, polymer blends, and/or polymer composites contemplated herein with one or more

optional antimicrobial agent(s) that either kill or slow the growth of microbes such as, but not limited to, antibacterial agents, antiviral agents, antifungal agents, antialgae agents and antiparasitic agents. These optional antimicrobial agents may be selected from any chemical compounds and polymers such as silicones containing silanol (SiOH), silicon hydride (SiH), carbinol (Si(CH₂)_xOH, where x = 1-18) and phenol; sulfonium compounds; phosphonium compounds; acids such as sorbic acid (vitamin C), citric acid, salicylic acid, fatty acids and derivatives, acetic acid, benzoic acid, tannic acid, gallic acid, octadecenedioic acid, hesperedin, glycyrrhizic acid, glycyrrhetic acid, n-acyl amino acid, hydroxyproline, niacin (vitamin B₃); aldehydes such as glutaraldehyde; alcohols such as erythritol, p-cymen-5-ol, p-cymen-7-ol, benzyl alcohol, phenol, thymol(2-isopropyl-5-methylphenol); 4-amino-N-(5-methyl-3-isoxazolyl) benzenesulfonamide; quaternary ammonium compounds (QACs) such as cetyl pyridinium chloride, Poly (hexamethylene biguanide) hydrochloride (PHMB); quinolone such as 8-hydroxyquinoline; carbendazim such as benzimidazole compounds, 2-benzimidazolecarbamoyl compounds; isothiazolinone derivatives such as n-butyl-1,2-benzisothiazolin-3-one (BBIT); methylisothiazolinone (MIT), chloromethylisothiazolinone (CMIT), benzisothiazolinone (BIT), octylisothiazolinone (OIT), dichlorooctylisothiazolinone (DCOIT), 2-n-octyl-4-isothiazolin-3-one (OBIT), 4-(1-methyl-1-mesitylcyclobutane-3-yl)-2-(2-hydroxy-3-methoxybenzylidenehydrazino)thiazole; hexahydro-1,3,5-tris-hydroxyethyl-s-triazine (HHT); chitosan, chitin; halogen-containing compounds such as chlorothalonil (tetrachloro-isophthalonitrile, CHTL), 2-bromo-2-nitropropane-1,3-diol (BNP), 3-iodo-2-propynyl-n-butylcarbamate (IPBC); metal-containing compounds or alloys such as copper (Cu), zinc (Zn) such as ZPT (zinc pyrithione), tin (Sn), gold (Au); 7-formylanil-substituted-imino-4-(4-methyl-2-butanone)-8-hydroxyquinoline-5-sulphonic acid complexes of cobalt, nickel or copper; As-containing compounds such as 10, 10'-oxybisphenoxyarsine (OBPA); sodium pyrithione (NaPT); and proteins such as lactoferrin. The antimicrobial agent can be dispersed into the formulation of the one or more polymers, polymer blends, and/or polymer composites in combination with other active agents such as antioxidants, UV absorbing agents, combinations thereof, and the like.

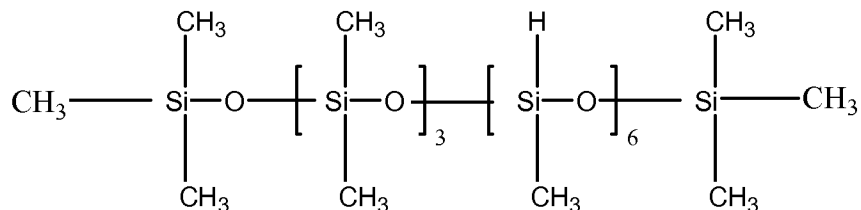
EXAMPLES

[0052] The examples below are intended to illustrate the embodiments of the present invention to one of ordinary skill in the art and should not be interpreted as limiting the scope of the invention set forth in the claims.

[0053] "M^{Vi}D₁₄₉M^{Vi'}", as referenced in the Examples below, was obtained from Dow Corning Corporation and has the chemical formula:



[0054] “MD₃D^H₆M”, as referenced in the Examples below, was obtained from Dow Corning Corporation and has the chemical formula:



Example 1 – Preparation of Hydrophilic Silicone Polymer (HSP) Liquid: Silicone-polyDADMAC HSP

[0055] A silicone-poly(diallyldimethyl ammonium chloride) HSP liquid was prepared using a reaction procedure, as described below. About 40.05g of vinyl-terminated polydimethylsiloxane (M^{Vi}D₁₄₉M^{Vi}) was combined with about 58.86g of D/T-vinyl siloxane, (M_{0.025}D_{0.913}T_{0.054}M^{Vi}_{0.08} having about 91.3 mol% D, about 2.5 mol% M, about 5.4 mol% T, about 0.8 mol% Me₂Vi), and a mixture of liquid monomers including about 51.69g diallyldimethyl ammonium chloride (DADMAC) (about 65 wt% DADMAC solution in water, purchased from Sigma-Aldrich, St. Louis, MO) and about 0.65g poly(ethylene glycol) dimethacrylate, Mn=550 (PEGDMA-550) crosslinker in the presence of about 0.294g peroxide initiator. The peroxide initiator was formed by combining about 0.294g of benzyl peroxide (BPO) with about 0.924g THF. The mixture was dispersed into an aqueous solution including about 39.01g of about 1wt% TERGITOL® 15-5-9 (Dow Chemical Co.) in a flask to form a cloudy liquid mixture. The water to silicone ratio was about 42.8/100 w/w.

[0056] The mixture was then nitrogen purged for about 10 minutes to remove oxygen and allowed to react/polymerize at about 86°C ± 2°C for about 4.5 hours. After the polymerization was completed, water and other volatile materials were removed at a temperature of about 71°C ± 2°C under a reduced pressure of about 10 mm Hg for about 1 hour. A white, unclear, and uniform liquid was obtained, which, after three months at room temperature, did not visibly separate. In this resulting hydrophilic silicone polymer with reactive vinyl groups in its molecules, DADMAC was into uniformly dispersed into the silicone network as polymer and copolymers with an interpenetrating polymer network (IPN) structure.

[0057] The present Example illustrates that although DADMAC is generally incompatible with silicone, it can, in fact, be incorporated into silicones to obtain a stable, hydrophilic, antimicrobial hybrid silicone.

Example 2 – Preparation of Hydrophilic Silicone Polymer (HSP) Liquid: Silicone-polyHEMA

[0058] A silicone-poly-2-hydroxyethyl methacrylate HSP liquid was prepared using a reaction procedure, as described below. About 175.47g of vinyl-terminated polydimethylsiloxane and liquid monomers of about 69.8g of 2-hydroxyethyl methacrylate (2-HEMA) and about 0.68g of PEGDMA-550 in the presence of about 0.54g of peroxide initiator were dispersed into about 140.45g of isopropanol (IPA) in a flask to form a cloudy, liquid mixture. The mixture was then nitrogen purged for about 10 minutes and allowed to react at about 85°C for about 3.5 hours. After the polymerization was completed, IPA and other volatile materials were removed at a temperature of about 75°C ± 2°C under a reduced pressure of about 10mm Hg. A white, unclear, and uniform liquid with an interpenetrating polymer network (IPN) structure was obtained, which after one week, did not visibly separate.

[0059] HEMA was introduced into silicone by this reaction, which resulted in HEMA becoming more stable and more uniformly distributed into silicone in its polymer and copolymers. Moreover, the resulting hydrophilic silicone-polyHEMA (HSP) polymer liquid may form a compatible mixture with other silicone liquids and then be cured into a gel or elastomer film, sheet, or coating on a solid substrate using the above-described method, which requires less time than allowing HEMA to be absorbed by silicone and then cured.

Example 3 – Preparation of Hydrophilic Silicone Elastomer

[0060] A hydrophilic silicone elastomer was prepared by curing a silicone-polyDADMAC HSP liquid (e.g., the silicone-polyDADMAC HSP liquid of Example 1 above). A liquid having the following components (and weight ratios) was prepared: silicone-polyDADMAC HSP liquid (about 100), dimethylhydopolysiloxane (MD₃D^H₆M, about 10.), and platinum divinyl-tetramethyldisiloxane catalyst (about 1). The liquid was mixed into a dental cup at in a rotary mixer (SPEEDMIXER™ DAC 150 FVZ (FlackTek Inc., Landrum, SC)) at a spinning speed of about 3540 rpm for about 20 seconds and then cured at a temperature of about 120°C for about 2 hours. The resulting HSP elastomer had a water absorption at room temperature by immersion of about 117.2 wt%/24 hr and about 980.2wt%/1 month. Thus, the resulting HSP elastomer was a superabsorbent and soft elastomer.

[0061] In addition to the antimicrobial activity of the resulting hydrophilic silicone elastomer, its hydrophilic nature allowed the elastomer to promote wound healing by providing a moist environment, while removing excess exudate and toxic components.

Example 4 – Preparation of Hydrophilic Silicone Elastomer

[0062] A hydrophilic silicone elastomer was prepared from silicone-polyHEMA HSP liquid (e.g., the silicone-polyHEMA HSP liquid of Example 2 above). A liquid having the following components (and weight ratios) was prepared: silicone-polyHEMA HSP liquid (about 100), dimethylhydropolysiloxane (about 15), and platinum divinyl-tetramethyldisilicone catalyst (about 0.08). The liquid was mixed into a dental cup at a speed of about 3540rpm for about 20 seconds and then cured at a temperature of about 120°C. The resulting HSP elastomer had a water absorption at room temperature by immersion of about 8.11 wt%/24 hour and about 16.9 wt%/2 months.

[0063] As evidenced by Example 4, although HEMA is not superabsorbent, it could still be used successfully to form a hydrophilic silicone gel/elastomer according to the embodiments discussed herein. Using HEMA may be desirable due to its popularity and ease of availability in healthcare applications. In contrast, although DADMAC formed a superabsorbent, it may be difficult to obtain.

[0064] This resulting HEMA-silicone elastomer is biocompatible and also miscible with common antimicrobial agents via the addition of such antimicrobial agents into its formulation. Its hydrophilic nature allowed the elastomer to promote wound healing by providing a moist environment, while removing excess exudate and toxic components.

Example 5 – Preparation of Antimicrobial Silicone Elastomer

[0065] Formulations of antimicrobial elastomers using the hydrophilic silicones prepared using the procedures described in the Examples above are summarized in Table 1 below.

Table 1

Sample	Formulation	Antimicrobial additive (weight)
1	HSP of Example 3	none
2	100g HSP of Example 3	5g of 20wt% Ag coated on E-powder
3	HSP of Example 4	None
4	100g HSP of Example 4	1g of Ag ₂ SO ₄ powder (mean size of about 4.82µm)
5	100g HSP of Example 4	5g of Ag ₂ SO ₄ powder coated on DOW CORNING® Trefil E-521 E-powder
6	100g HSP of Example 4	4g of AgNO ₃ on DOW CORNING® Trefil E-521 E-powder

[0066] About 9.50g of the obtained silicone liquid mixtures were poured into a glass dish (100 × 20 mm) and then instantly put into an oven at about 150°C for about 5-10 minutes to be cured into a silicone elastomeric film with a thickness of about 1.2mm for antimicrobial testing. The antimicrobial testing was in accordance with ASTM E2149-10. The antimicrobial testing results for the samples of Table 1 are provided in Table 2 below.

Table 2

Sample	ASTM E2149-10 log reduction	Zone-of-Inhibition (ZOI)
1	4.7	none
2	4.7	zone
3	0.6	none
4	0.4	none
5	0.1	none
6	4.8	none

[0067] As shown in Table 2, the hydrophilic silicone elastomer prepared from DADMAC showed good antimicrobial activity even without additional antimicrobial agent. On the other hand, the hydrophilic silicone elastomer prepared from HEMA initially had no antimicrobial activity, but this was greatly improved in the presence of AgNO₃ on DOW CORNING® Trefil E-521 E-powder as the antimicrobial agent.

[0068] While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the examples and described in detail herein. It should be understood, however, that the invention is not intended to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A method of preparing a hydrophilic hybrid silicone polymer, the method comprising:
 - (i) combining (a) a silicone having one or more reactive or polymerizable groups and (b) at least one hydrophilic monomer in the presence of (c) at least one initiator to form a mixture; and
 - (ii) polymerizing the mixture from (i) to form the hydrophilic hybrid silicone polymer.
2. The method of claim 1, wherein the initiator (c) is a catalyst configured to initiate polymerization of the silicone, polymerization of the hydrophilic monomer, and/or the copolymerization of the silicone and the hydrophilic monomer, and is selected from a free radical initiator, a condensation catalyst, a photoinitiator, or any combination thereof.
3. The method of any of claims 1-2, wherein the hydrophilic hybrid silicone polymer comprises a copolymer of the hydrophilic monomer and silicone, a homopolymer of the hydrophilic monomer and silicone, or a combination thereof.
4. The method of any of claims 1-3, wherein the one or more reactive or polymerizable groups comprises (i) one or more functional groups configured to be reacted or polymerized to form longer chains and/or a crosslinked network or (ii) one or more unsaturated hydrocarbon functional groups.
5. The method of any of claims 1-4, wherein the hydrophilic monomer includes vinyl, allyl, acrylates or alkylacrylates and hydroxyl, poly(ethylene glycol), ether, cyano, carboxyl groups, for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, (3-acryloyloxy)-2-hydroxypropyl methacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(ethylene glycol) dimethacrylate, 2-cyanoethyl acrylate, β -carboxyethyl acrylate vinyl ethyl ether, vinyl phenyl ether, diallyl maleate, or any combination thereof.
6. The method of any of claims 1-5, wherein the silicone and the at least one hydrophilic monomer are further combined in the presence of an aqueous solution comprising water, isopropanol, tetrahydrofuran, acetone, or any combination thereof.
7. A hydrophilic hybrid silicone polymer prepared the method of any of claims 1-6.
8. The hydrophilic hybrid silicone polymer of claim 7, wherein the hydrophilic hybrid silicone polymer is a liquid that does not visibly separate after three days at room temperature.
9. A method of forming a hydrophilic silicone elastomer, the method comprising:
 - (i) combining silicone and at least one hydrophilic monomer in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups; and

- (ii) further reacting the hydrophilic hybrid silicone polymer of (i) with one or more reactive groups to form the hydrophilic silicone elastomer.
10. The method of claim 9, wherein the act of further reacting comprises curing or solidification through physicochemical methods, the physicochemical methods including light, UV exposure, heating/cooling, radiation, moisture, ozone, high pressure, low pressure, magnetic fields, electric fields, or any combination thereof.
11. A method of forming a hydrophilic silicone elastomer, the method comprising:
- (i) combining silicone and at least one hydrophilic monomer in the presence of at least one initiator to form a hydrophilic hybrid silicone polymer, the silicone including one or more reactive or polymerizable groups; and
- (ii) dispersing the hydrophilic hybrid silicone polymer of (i) into a silicone matrix, the silicone matrix being formed by reacting (a) silicone with unsaturated hydrocarbon functional groups with (b) silicone hydride groups in the presence of a hydrolisation catalyst.
12. The method of claim 11, wherein the hydrophilic hybrid silicone polymer is a liquid or a solid powder.
13. The method of any of claims 9-12, wherein the hydrophilic monomer is diallyldimethyl ammonium chloride, other quaternary salts, acrylamide derivatives, or a combination thereof.
14. A hydrophilic silicone elastomer prepared by the method of any of claims 9-13.
15. A hydrophilic hybrid silicone polymer liquid comprising:
- at least one silicone polymerized with at least one hydrophilic monomer, the at least one hydrophilic monomer including diallyldimethyl ammonium chloride, other quaternary salts, acrylamide derivatives, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/025878

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G77/42 C08F283/12 C08F290/14 C08L83/10
 ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C08G C08F C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/029111 A1 (CHANG FRANK [US] ET AL) 2 February 2012 (2012-02-02) examples 2,3	1-15
X	WO 2008/095822 A2 (CIBA HOLDING INC [CH]; KOROSKENYI BALINT [US]; GAMEZ-GARCIA MANUEL [US] 14 August 2008 (2008-08-14) example 4 page 6, lines 1-2	1-15
X	DE 10 2005 018315 A1 (RUDOLF GMBH & CO KG CHEM FAB [DE]) 2 November 2006 (2006-11-02) example 3	1-8,11, 12,15
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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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 May 2014	Date of mailing of the international search report 28/05/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Queste, Sébastien

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/025878

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 779 318 A1 (WAKO PURE CHEMICAL INDUSTRIES L [JP]) 18 June 1997 (1997-06-18) example 5 -----	1-8,11, 12,15
X	US 2010/010165 A1 (HASHEMZADEH ABDULMAJID [DE]) 14 January 2010 (2010-01-14) paragraph [0036]; example 2 -----	1-8,11, 12,15
X,P	WO 2013/096332 A1 (DOW CORNING [US]; DOW CORNING TAIWAN INC) 27 June 2013 (2013-06-27) paragraphs [0006], [0014], [0020], [0022], [0028], [0029], [0038], [0040], [0047] example 1 -----	1-8
X,P	EP 2 599 847 A1 (DOW CORNING [US]; DOW CORNING FRANCE SAS [FR]) 5 June 2013 (2013-06-05) paragraphs [0002], [0015], [0019], [0020], [0045], [0052], [0054], [0057] example 7 -----	1-10, 13-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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