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(54) **MALEIMIDE-TERMINATED SULFUR-CONTAINING POLYMERS, COMPOSITIONS THEREOF, AND USES THEREOF**

MALEIMIDTERMINIERTE SCHWEFELHALTIGE POLYMERE, ZUSAMMENSETZUNGEN DARAUS UND VERWENDUNGEN DAVON

POLYMERES SOUFRES A TERMINAISON MALEIMIDE, COMPOSITIONS DESDITS POLYMERES, ET LEURS UTILISATION

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Description**FIELD**

[0001] The present disclosure relates to maleimide-terminated sulfur-containing polymers such as maleimide-terminated polythioethers, polysulfides, and sulfur-containing polyformals useful in aerospace sealant applications. The disclosure also relates to sulfur-containing maleimide adducts having terminal 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione groups and compositions thereof.

BACKGROUND

[0002] Sealants useful in aerospace and other applications must satisfy demanding mechanical, chemical, and environmental requirements. The sealants can be applied to a variety of surfaces including metal surfaces, primer coatings, intermediate coatings, finished coatings, and aged coatings. Cured sealants having increased tensile strength and elongation and that also meet other requirements of aerospace sealants such as fuel resistance are desired.

[0003] US 2012/0040103 discloses compositions that include a thiol-terminated polymer and a sulfur-containing ethylenically unsaturated silane.

[0004] US 2004/0247792 relates to polythioether polymers, curable compositions containing same, the process of making polythioether polymers and their use in sealants.

[0005] US 2011/0319559 describes polythioethers that are the reaction product of reactants that include a) an isocyanurate-containing trithiol, b) a polythiol different from a) and c) a diene.

[0006] US 2003/0008977 relates to sealants and potting formulations which are prepared from components including ungelled mercapto-terminated polymers prepared by reacting reactants comprising polyvinyl ether monomers and polythiol materials; curing agents reactive with a mercapto group of the mercapto-terminated polymer and additives selected from fillers, adhesion promoters plasticizers and catalyst.

[0007] US 5,912,319 discloses compositions and methods for producing fuel resistant liquid polythioether polymers with good low temperature flexibility.

[0008] US 2015/0119549 describes sulfur-containing polymers and sulfur containing adducts having terminal 1,1'-(methylene-4,1-phenylene)bismaleimide groups.

SUMMARY

[0009] In a first aspect, sulfur-containing maleimide adducts comprising at least two terminal maleimide groups are provided.

[0010] In a second aspect, compositions are provided comprising (a) a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups; and (b) a compound having at least two maleimide groups.

[0011] In a third aspect, compositions are provided comprising (a) a sulfur-containing maleimide adduct; and (b) a curing agent comprising at least two terminal groups that are reactive with maleimide groups.

[0012] In a fourth aspect, compositions are provided comprising (a) a sulfur-containing maleimide adduct; (b) a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups; and (c) a monomeric compound having at least two maleimide groups.

[0013] In a fifth aspect, compositions comprising a sulfur-containing maleimide adduct, formulated as a sealant, are provided.

[0014] In a sixth aspect, cured sealants comprising a composition comprising a sulfur-containing maleimide adduct, formulated as a sealant, are provided.

DETAILED DESCRIPTION**Definitions**

[0015] "Alkanediyl" refers to a diradical of a saturated, branched or straight-chain, acyclic hydrocarbon group, having, for example, from 1 to 18 carbon atoms (C_{1-18}), from 1 to 14 carbon atoms (C_{1-14}), from 1 to 6 carbon atoms (C_{1-6}), from 1 to 4 carbon atoms (C_{1-4}), or from 1 to 3 hydrocarbon atoms (C_{1-3}). It will be appreciated that a branched alkanediyl has a minimum of three carbon atoms. In certain embodiments, the alkanediyl is C_{2-14} alkanediyl, C_{2-10} alkanediyl, C_{2-8} alkanediyl, C_{2-6} alkanediyl, C_{2-4} alkanediyl, and in certain embodiments, C_{2-3} alkanediyl. Examples of alkanediyl groups include methane-diyl ($-CH_2-$), ethane-1,2-diyl ($-CH_2CH_2-$), propane-1,3-diyl and iso-propane-1,2-diyl (e.g., $-CH_2CH_2CH_2-$ and $-CH(CH_3)CH_2-$), butane-1,4-diyl ($-CH_2CH_2CH_2CH_2-$), pentane-1,5-diyl ($-CH_2CH_2CH_2CH_2CH_2-$), hexane-1,6-diyl ($-CH_2CH_2CH_2CH_2CH_2CH_2-$), heptane-1,7-diyl, octane-1,8-diyl, nonane-1,9-diyl, decane-1,10-diyl, dodecane-1,12-diyl,

and the like.

[0016] "Alkanecycloalkane" refers to a saturated hydrocarbon group having one or more cycloalkyl and/or cycloalkanediyl groups and one or more alkyl and/or alkanediyl groups, where cycloalkyl, cycloalkanediyl, alkyl, and alkanediyl are defined herein. In certain embodiments, each cycloalkyl and/or cycloalkanediyl group(s) is C₃₋₆, C₅₋₆, and in certain embodiments, cyclohexyl or cyclohexanediyl. In certain embodiments, each alkyl and/or alkanediyl group(s) is C₁₋₆, C₁₋₄, C₁₋₃, and in certain embodiments, methyl, methanediyl, ethyl, or ethane-1,2-diyl. In certain embodiments, the alkanecycloalkane group is C₄₋₁₈ alkanecycloalkane, C₄₋₁₆ alkanecycloalkane, C₄₋₁₂ alkanecycloalkane, C₄₋₈ alkanecycloalkane, C₆₋₁₂ alkanecycloalkane, C₆₋₁₀ alkanecycloalkane, and in certain embodiments, C₆₋₉ alkanecycloalkane. Examples of alkanecycloalkane groups include 1,1,3,3-tetramethylcyclohexane and cyclohexylmethane.

[0017] "Alkanecycloalkanediyl" refers to a diradical of an alkanecycloalkane group. In certain embodiments, the alkanecycloalkanediyl group is C₄₋₁₈ alkanecycloalkanediyl, C₄₋₁₆ alkanecycloalkanediyl, C₄₋₁₂ alkanecycloalkanediyl, C₄₋₈ alkanecycloalkanediyl, C₆₋₁₂ alkanecycloalkanediyl, C₆₋₁₀ alkanecycloalkanediyl, and in certain embodiments, C₆₋₉ alkanecycloalkanediyl. Examples of alkanecycloalkanediyl groups include 1,1,3,3-tetramethylcyclohexane-1,5-diyl and cyclohexylmethane-4,4'-diyl.

[0018] "Alkanearene" refers to a hydrocarbon group having one or more aryl and/or arenediyl groups and one or more alkyl and/or alkanediyl groups, where aryl, arenediyl, alkyl, and alkanediyl are defined herein. In certain embodiments, each aryl and/or arenediyl group(s) is C₆₋₁₂, C₆₋₁₀, and in certain embodiments, phenyl or benzenediyl. In certain embodiments, each alkyl and/or alkanediyl group(s) is C₁₋₆, C₁₋₄, C₁₋₃, and in certain embodiments, methyl, methanediyl, ethyl, or ethane-1,2-diyl. In certain embodiments, the alkanearene group is C₄₋₁₈ alkanearene, C₄₋₁₆ alkanearene, C₄₋₁₂ alkanearene, C₄₋₈ alkanearene, C₆₋₁₂ alkanearene, C₆₋₁₀ alkanearene, and in certain embodiments, C₆₋₉ alkanearene. Examples of alkanearene groups include diphenyl methane.

[0019] "Alkanearenediyl" refers to a diradical of an alkanearene group. In certain embodiments, the alkanearenediyl group is C₄₋₁₈ alkanearenediyl, C₄₋₁₆ alkanearenediyl, C₄₋₁₂ alkanearenediyl, C₄₋₈ alkanearenediyl, C₆₋₁₂ alkanearenediyl, C₆₋₁₀ alkanearenediyl, and in certain embodiments, C₆₋₉ alkanearenediyl. Examples of alkanearenediyl groups include diphenyl methane-4,4'-diyl.

[0020] "Alkenyl" group refers to a group having the structure -RC=C(R)₂ where the alkenyl group is a terminal group and is bonded to a larger molecule. In such embodiments, each R may be selected from, for example, hydrogen and C₁₋₃ alkyl. In certain embodiments, each R is hydrogen and an alkenyl group has the structure -CH=CH₂.

[0021] "Alkoxy" refers to a -OR group where R is alkyl as defined herein. Examples of alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, and n-butoxy. In certain embodiments, the alkoxy group is C₁₋₈ alkoxy, C₁₋₆ alkoxy, C₁₋₄ alkoxy, and in certain embodiments, C₁₋₃ alkoxy.

[0022] "Alkyl" refers to a monoradical of a saturated, branched or straight-chain, acyclic hydrocarbon group having, for example, from 1 to 20 carbon atoms, from 1 to 10 carbon atoms, from 1 to 6 carbon atoms, from 1 to 4 carbon atoms, or from 1 to 3 carbon atoms. It will be appreciated that a branched alkyl has a minimum of three carbon atoms. In certain embodiments, the alkyl group is C₁₋₆ alkyl, C₁₋₄ alkyl, and in certain embodiments, C₁₋₃ alkyl. Examples of alkyl groups include methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-hexyl, n-decyl, tetradecyl, and the like. In certain embodiments, the alkyl group is C₁₋₆ alkyl, C₁₋₄ alkyl, and in certain embodiments, C₁₋₃ alkyl. It will be appreciated that a branched alkyl has at least three carbon atoms.

[0023] "Arenediyl" refers to diradical monocyclic or polycyclic aromatic group. Examples of arenediyl groups include benzene-diyl and naphthalene-diyl. In certain embodiments, the arenediyl group is C₆₋₁₂ arenediyl, C₆₋₁₀ arenediyl, C₆₋₉ arenediyl, and in

[0024] "Cycloalkanediyl" refers to a diradical saturated monocyclic or polycyclic hydrocarbon group. In certain embodiments, the cycloalkanediyl group is C₃₋₁₂ cycloalkanediyl, C₃₋₈ cycloalkanediyl, C₃₋₆ cycloalkanediyl, and in certain embodiments, C₅₋₆ cycloalkanediyl. Examples of cycloalkanediyl groups include cyclohexane-1,4-diyl, cyclohexane-1,3-diyl, and cyclohexane-1,2-diyl.

[0025] "Cycloalkyl" refers to a saturated monocyclic or polycyclic hydrocarbon monoradical group. In certain embodiments, the cycloalkyl group is C₃₋₁₂ cycloalkyl, C₃₋₈ cycloalkyl, C₃₋₆ cycloalkyl, and in certain embodiments, C₅₋₆ cycloalkyl.

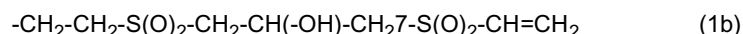
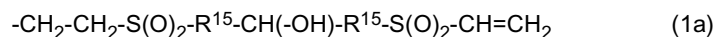
[0026] "Heteroalkanediyl" refers to an alkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanediyl, the heteroatom is selected from N and O.

[0027] "Heterocycloalkanediyl" refers to a cycloalkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heterocycloalkanediyl, the heteroatom is selected from N and O.

[0028] "Heteroarenediyl" refers to an arenediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroarenediyl, the heteroatom is selected from N and O.

[0029] "Heterocycloalkanediyl" refers to a cycloalkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heterocycloalkanediyl, the heteroatom is selected from N and O.

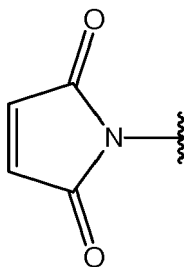
[0030] A "Michael acceptor" refers to substituted alkene/alkyne compounds in which at least one alkene/alkyne group is directly attached to one or more electron-withdrawing group such as carbonyl (-CO), nitro (-NO₂), nitrile (-CN), alkoxycarbonyl (-COOR), phosphonate (-PO(OR)₂), trifluoromethyl (-CF₃), sulfonyl (-SO₂-), trifluoromethanesulfonyl (-SO₂CF₃), p-toluenesulfonyl (-SO₂-C₆H₄-CH₃), etc. Types of compounds that function as Michael acceptors are vinyl ketones, quinones, nitroalkenes, acrylonitriles, acrylates, methacrylates, cyanoacrylates, acrylamides, maleimides, dialkyl vinylphosphonate, and vinylsulfones. Other examples of Michael acceptors are disclosed in Mather et al., Prog. Polym. Sci. 2006, 31, 487-531. Michael acceptor compounds having more than one Michael acceptor group are also well known. Examples include diacrylates such as ethylene glycol diacrylate and diethylene glycol diacrylate, dimethacrylates such as ethylene glycol methacrylate and diethylene glycol methacrylate, bismaleimides such as N,N'-(1,3-phenylene)dimalimide and 1,1'-(methylenedi-4,1-phenylene)bismaleimide, vinylsulfones such as divinyl sulfone and 1,3-bis(vinylsulfonyl)-2-propanol, etc. In certain embodiments, a Michael acceptor group has the structure of Formula (1a) or Formula (1b):



where each R¹⁵ is independently selected from C₁₋₃ alkanediyl and substituted C₁₋₃ alkanediyl, wherein the one or more substituent groups is -OH.

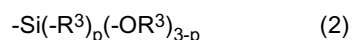
[0031] A "Michael acceptor compound" refers to a compound comprising at least one terminal Michael acceptor group. In certain embodiments, a Michael acceptor compound is divinyl sulfone, and a Michael acceptor group is vinylsulfonyl, i.e., -S(O)₂-CH=CH₂. In certain embodiments, a Michael acceptor compound is a bis(vinylsulfonyl)alkanol, and a Michael acceptor group is 1-(ethylenesulfonyl)-n-(vinylsulfonyl)alkanol, i.e., -CH₂-CH₂-S(O)₂-R¹⁰-CH(OH)-R¹⁰-S(O)₂-CH=CH₂, and in certain embodiments, 1-(ethylenesulfonyl)-3-(vinylsulfonyl)propan-2-ol (CH₂-CH₂-S(O)₂-CH₂-CH(OH)-CH₂-S(O)₂-CH=CH₂). In certain embodiments, a Michael acceptor group is a maleimide and in certain embodiments, a 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione group.

[0032] A "maleimide" refers to a compound having a maleimide group:



[0033] A bismaleimide refers to a compound having two maleimide groups, where the two maleimide groups are bonded by the nitrogen atoms via a linker.

[0034] A "polyalkoxysilyl group" refers to a group having the structure of Formula (2):



where p is selected from 0, 1, and 2; and each R³ is independently selected from C₁₋₄ alkyl. In certain embodiments of a polyalkoxysilyl group, p is 0, p is 1, and in certain embodiments, p is 2. In certain embodiments of a polyalkoxysilyl group, each R³ is independently selected from ethyl and methyl. In certain embodiments of a polyalkoxysilyl group, each R³ is ethyl, and in certain embodiments, each R³ is methyl. In certain embodiments of a polyalkoxysilyl group, the group is selected from -Si(-OCH₂CH₃)₃, -Si(-OCH₃)₃, -Si(-CH₃)(-OCH₃)₂, -Si(-CH₃)₂(-OCH₃), -Si(-CH₃)(-OCH₂CH₃)₂, -Si(-CH₃)₂(-OCH₂CH₃), -Si(-CH₂CH₃)(-OCH₃), and -Si(-CH₂CH₃)₂(-OCH₃).

[0035] As used herein, "polymer" refers to oligomers, homopolymers, and copolymers. Unless stated otherwise, molecular weights are number average molecular weights for polymeric materials indicated as "Mn" as determined, for example, by gel permeation chromatography using a polystyrene standard in an art-recognized manner.

[0036] "Substituted" refers to a group in which one or more hydrogen atoms are each independently replaced with the same or different substituent(s). In certain embodiments, the substituent is selected from halogen, -S(O)₂OH, -S(O)₂, -SH, -SR where R is C₁₋₆ alkyl, -COOH, -NO₂, -NR₂ where each R is independently selected from hydrogen and C₁₋₃ alkyl, -CN, =O, C₁₋₆ alkyl, -CF₃, -OH, phenyl, C₂₋₆ heteroalkyl, C₅₋₆ heteroaryl, C₁₋₆ alkoxy, and -COR where R is C₁₋₆ alkyl. In certain embodiments, the substituent is chosen from -OH, -NH₂, and C₁₋₃ alkyl. In certain embodiments, the

substituent is chosen from -OH and C₁₋₃ alkyl, and in certain embodiments the one or more substituent group is -OH.

[0037] Reference is now made to certain embodiments of sulfur-containing adducts having terminal maleimide groups, prepolymers, polymers, compositions, and methods. The disclosed embodiments are not intended to be limiting of the claims. To the contrary, the claims are intended to cover all alternatives, modifications, and equivalents.

Sulfur-containing Maleimide Adducts

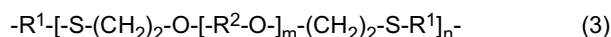
[0038] Sulfur-containing maleimide adducts provided by the present disclosure comprise at least two terminal maleimide groups. Sulfur-containing prepolymers and adducts include, for example, polythioethers, polysulfides, sulfur-containing polyformals, and combinations thereof. Examples of suitable polythioethers are disclosed, for example, in U.S. Patent No. 6,123,179. Examples of suitable polysulfides are disclosed, for example, in U.S. Patent No. 4,623,711. In certain embodiments, a sulfur-containing maleimide adduct may be difunctional, and in certain embodiments, may have a functionality greater than 2 such as 3, 4, 5, or 6. A sulfur-containing maleimide adduct may comprise a mixture of sulfur-containing maleimide adducts having different functionalities characterized by an average functionality from 2.05 to 6, from 2.1 to 4, from 2.1 to 3, from 2.2 to 2.8, and in certain embodiments, from 2.4 to 2.6. Sulfur-containing maleimide adducts have at least two terminal maleimide groups, and in certain embodiments have two terminal 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione groups, and in certain embodiments have more than two terminal groups such as 3, 4, 5, or 6 terminal 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione groups. A sulfur-containing maleimide adduct may comprise a combination of adducts having different numbers of terminal 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione groups characterized, for example, by an average 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione functionality from 2.05 to 6, from 2.1 to 4, from 2.1 to 3, from 2.2 to 2.8, and in certain embodiments, from 2.4 to 2.6.

[0039] The double bond of maleimides can react with thiol groups at pH 6.5 to 7.5 and is more reactive than (meth)acrylates. At neutral pH, the reaction of maleimides with thiols is about 1,000 times faster than the reaction of maleimides with amines. Advanced compositions prepared from maleimide resins exhibit excellent thermomechanical stability and anti-flammability.

[0040] In certain embodiments, a sulfur-containing maleimide adduct comprises a polythioether maleimide adduct characterized by a polythioether having at least two terminal maleimide groups such as, for example, at least two terminal 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione groups.

[0041] In certain embodiments, a sulfur-containing maleimide adduct comprises a polythioether maleimide adduct comprising:

(a) a backbone comprising the structure of Formula (3):



where (i) each R¹ is independently selected from a C₂₋₁₀ n-alkanediyl group, a C₃₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₆₋₁₀ alkanecycloalkanediyl group, a heterocyclic group, a -[(CHR³)_p-X]_q- (CHR³)_r- group, wherein each R³ is independently selected from hydrogen and methyl; (ii) each R² is independently selected from a C₂₋₁₀ n-alkanediyl group, a C₃₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₆₋₁₄ alkanecycloalkanediyl group, a heterocyclic group, and a -[(CH₂)_p-X]_q- (CH₂)_r- group; (iii) each X is independently selected from O, S, and a -NR⁶- group, in which R⁶ is selected from H and a methyl group; (iv) m ranges from 0 to 50; (v) n is an integer ranging from 1 to 60; (vi) p is an integer ranging from 2 to 6; (vii) q is an integer ranging from 1 to 5; and (viii) r is an integer ranging from 2 to 10; and

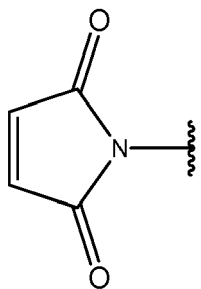
(b) at least two terminal maleimide groups.

[0042] In certain embodiments of a compound of Formula (3), R¹ is -[(CHR³)_s-X]_q-(CHR³)_r- wherein each X is independently selected from -O- and -S-. In certain embodiments wherein R¹ is -[(CHR³)_s-X]_q-(CHR³)_r-, each X is -O- and in certain embodiments, each X is -S-.

[0043] In certain embodiments of a compound of Formula (3), R¹ is -[(CH₂)_s-X]_q-(CH₂)_r- wherein each X is independently selected from -O- and -S-. In certain embodiments wherein R¹ is -[(CH₂)_s-X]_q-(CH₂)_r-, each X is -O- and in certain embodiments, each X is -S-.

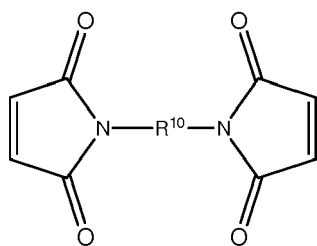
[0044] In certain embodiments, R¹ in Formula (3) is -[(CH₂)_p-X]_q-(CH₂)_r-, where p is 2, X is O, q is 2, r is 2, R² is ethanediyl, m is 2, and n is 9.

[0045] A terminal maleimide group has the structure of Formula (4):



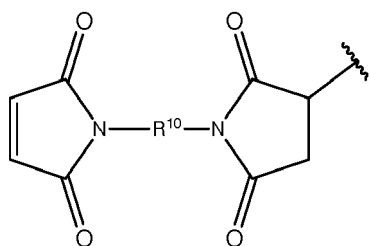
(4)

[0046] A terminal bismaleimide moiety refers to a moiety having a terminal maleimide group. In certain embodiments, a terminal maleimide group is derived from a bismaleimide, such as a compound having the structure of Formula (5a):



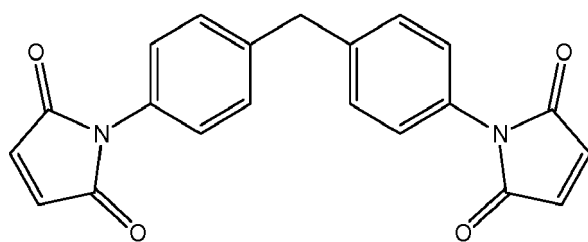
(5a)

where R^{10} is a divalent organic moiety, and the terminal group has the structure of Formula (5b):

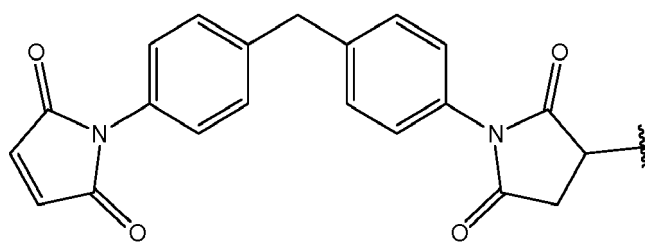


(5b)

and is referred to herein as a 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione group. In certain embodiments, a terminal maleimide group is derived from 1,1'-(methylenedi-4,1-phenylene)bismaleimide of Formula (7a), also referred to as 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione), and the terminal group has the structure of Formula (7b):



(7a)

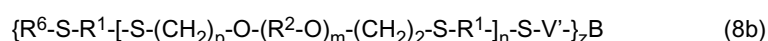
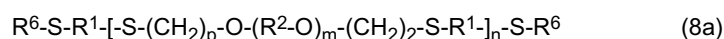


(7b)

[0047] In certain embodiments, a maleimide group comprises 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione group. In certain embodiments, each of the terminal maleimide groups may be the same and in certain embodiments, at least some of the terminal maleimide groups are different.

[0048] Other examples of compounds having two or more maleimide groups include ethylenebismaleimide; 1,6-bis-maleimidohexane; 2,4-dimaleimidotoluene, N,N'-1,3-phenylenedimaleimide; 1,4-bis(maleimido)butane trimethylenebismaleimide; p,p'-dimaleimidodiphenylmethane; pentamethylenebismaleimide 1H-pyrrole-2,5-dione; 1,1'-(1,8-octanediyl)bis-, 1H-pyrrole-2,5-dione, 1,1'-(1,7-heptanediyl)bis-, 4,4'-dithiobis(phenylmaleimide); methylenebis(N-carbamylmaleimide), 1,9-bis(maleimide)nonane; 1,1'-decane-1,10-diylbis(1H-pyrrole-2,5-dione); O-phenylene dimaleimide, bis(N-maleimidomethyl)ether; 1,5-bis(maleimide)-2-methyl-pentane; N,N'-1,4-phenylenedimaleimide; 1,1'-(2-methyl-1,3-phenylene)bis(1H-pyrrole-2,5-dione); Kerimid 601 resin; tetrakis(N-2-aminoethylmaleamide); 1-(2,5-dimethylphenyl)pyrrole-2,5-dione; SureCN331305, SureCN349749; or 1,1'-biphenyl-4,4'-diylbis(1H-pyrrole-2,5-dione).

[0049] In certain embodiments where the sulfur-containing maleimide adduct comprises a polythioether maleimide adduct, the polythioether maleimide adduct is selected from a polythioether maleimide adduct of Formula (8a), a polythioether maleimide adduct of Formula (8b), and a combination thereof:



wherein:

each R^1 independently is selected from C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, and $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein:

s is an integer from 2 to 6;

q is an integer from 1 to 5;

r is an integer from 2 to 10;

each R^3 is independently selected from hydrogen and methyl; and

each X is independently selected from -O-, -S-, and -NR-, wherein

R is selected from hydrogen and methyl;

each R^2 is independently selected from C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, and $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein s, q, r, R^3 , and X are as defined for R^1 ;

m is an integer from 0 to 50;

n is an integer from 1 to 60;

p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent $B(\square V)_z$ wherein:

z is an integer from 3 to 6; and

each V is a group comprising a terminal group reactive with thiol groups; and

each -V'- is derived from the reaction of -V with a thiol; and

each R^6 is independently a moiety comprising a terminal maleimide group.

[0050] In certain embodiments of Formula (8a) and in Formula (8b), R^1 is $-[(CH_2)_p-X]_q-(CH_2)_r-$, where p is 2, X is -O-, q is 2, r is 2, R^2 is ethanediyl, m is 2, and n is 9.

[0051] In certain embodiments of Formula (8a) and Formula (8b), R^1 is selected from C_{2-6} alkanediyl and $-[(CHR^3)_s-X]_q-(CHR^3)_r-$.

[0052] In certain embodiments of Formula (8a) and Formula (8b), R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, and in certain embodiments X is -O- and in certain embodiments, X is -S-.

[0053] In certain embodiments of Formula (8a) and Formula (8b), where R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, p is 2, r is 2, q is 1, and X is -S-; in certain embodiments, wherein p is 2, q is 2, r is 2, and X is -O-; and in certain embodiments, p is 2, r is 2, q is 1, and X is -O-.

[0054] In certain embodiments of Formula (8a) and Formula (8b), where R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, each R^3 is hydrogen, and in certain embodiments, at least one R^3 is methyl.

[0055] In certain embodiment of adducts of Formula (8a) and Formula (8b), each R^1 is the same, and in certain embodiments, at least one R^1 is different.

[0056] In certain embodiments, each -V comprises a terminal alkenyl group.

[0057] In certain embodiments of adducts of Formula (8a) and Formula (8b), each R⁶ is independently derived from a bismaleimide. In certain embodiments, each of the terminal maleimide moieties may be the same and in certain embodiments, at least some of the terminal maleimide moieties are different.

[0058] In certain embodiments, each R⁶ is 1-(4-(4-(3-yl-2,5-dioxopyrrolidin-1-yl)benzyl)phenyl)-1H-pyrrole-2,5-dione.

[0059] In certain embodiments of adducts of Formula (8a) and Formula (8b), each R⁶ is derived from a bismaleimide such as 1,1'-(methylenebis(4,1-phenylene)bis(1H-pyrrole-2,5-dione). In certain embodiments, each R⁶ is derived from ethylenebismaleimide, 1,6-bismaleimidohexane, 2,4-dimaleimidotoluene, N,N'-1,3-phenylenedimaleimide; 1,4-bis(maleimido)butane trimethylenebismaleimide; p,p'-dimaleimidodiphenylmethane; pentamethylenebismaleimide 1H-pyrrole-2,5-dione; 1,1'-(1,8-octanediyl)bis-, 1H-pyrrole-2,5-dione, 1,1'-(1,7-heptanediyl)bis-, 4,4'-dithiobis(phenylmaleimide); methylenebis(N-carbamylmaleimide), 1,9-bis(maleimide)nonane; 1,1'-decane-1,10-diylbis(1H-pyrrole-2,5-dione); O-phenylene dimaleimide, bis(N-maleimidomethyl)ether; 1,5-bis(maleimide)-2-methyl-pentane; N,N'-1,4-phenylenedimaleimide; 1,1'-(2-methyl-1,3-phenylene)bis(1H-pyrrole-2,5-dione); Kerimid 601 resin; tetrakis(N-2-aminoethylmaleamide); 1-(2,5-dimethylphenyl)pyrrole-2,5-dione; SureCN331305; SureCN349749; or 1,1'-biphenyl-4,4'-diylbis(1H-pyrrole-2,5-dione).

[0060] In certain embodiments, a sulfur-containing maleimide adduct comprises a polysulfide adduct comprising at least two terminal maleimide groups.

[0061] As used herein, the term polysulfide refers to a polymer that contains one or more polysulfide linkages, i.e., -S_x- linkages, where x is from 2 to 4, in the polymer backbone and/or in pendant positions on the polymer chain. In certain embodiments, the polysulfide polymer will have two or more sulfur-sulfur linkages. Suitable polysulfides are commercially available, for example, from Akzo Nobel and Toray Fine Chemicals under the names Thiokol-LP and Thioplast®. Thioplast® products are available in a wide range of molecular weights ranging, for example, from less than 1,100 Daltons to over 8,000 Daltons, with molecular weight being the average molecular weight in grams per mole. In some cases, the polysulfide has a number average molecular weight of 1,000 Daltons to 4,000 Daltons. The crosslink density of these products also varies, depending on the amount of crosslinking agent used. The -SH content, i.e., thiol or mercaptan content, of these products can also vary. The mercaptan content and molecular weight of the polysulfide can affect the cure speed of the polymer, with cure speed increasing with molecular weight.

[0062] In certain embodiments, a sulfur-containing maleimide adduct comprises a polythioether maleimide comprising at least two terminal maleimide groups, a polysulfide adduct comprising at least two terminal maleimide groups, a sulfur-containing polyformal adduct comprising at least two terminal maleimide groups, or a combination of any of the foregoing.

[0063] Sulfur-containing polyformal prepolymers useful in aerospace sealant applications are disclosed, for example, in U.S. Application Publication No. 2012/0234205 and in U.S. Application Publication No. 2012/0238707.

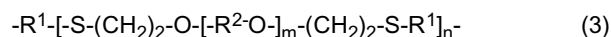
[0064] In certain embodiments, sulfur-containing maleimide adducts provided by the present disclosure comprise the reaction products of reactants comprising: (a) a sulfur-containing polymer; and (b) a compound having a terminal maleimide group and a group that is reactive with a terminal group of the sulfur-containing polymer.

[0065] In certain embodiments, the sulfur-containing polymer is selected from a polythioether, a polysulfide, a sulfur-containing polyformal, and a combination thereof. In certain embodiments a sulfur-containing polymer comprises a polythioether, and in certain embodiments, a sulfur-containing polymer comprises a polysulfide. A sulfur-containing polymer may comprise a mixture of different polythioethers and/or polysulfides, and the polythioethers and/or polysulfides may have the same or different functionality. In certain embodiments, a sulfur-containing polymer has an average functionality from 2 to 6, from 2 to 4, from 2 to 3, and in certain embodiments, from 2.05 to 2.5. For example, a sulfur-containing polymer can be selected from a difunctional sulfur-containing polymer, a trifunctional sulfur-containing polymer, and a combination of any of the foregoing. In certain embodiments, a sulfur-containing polymer can be selected from a sulfur-containing polyformal.

[0066] In certain embodiments, a sulfur-containing polymer comprises two or more terminal groups that are reactive with the terminal reactive group of the compound having a terminal maleimide group. In certain embodiments, the compound having a terminal maleimide group has two maleimide groups, and the terminal groups of the sulfur-containing polymer are reactive with maleimide groups. A sulfur-containing polymer may comprise terminal thiol groups or terminal epoxy groups.

[0067] In certain embodiments, a sulfur-containing polymer is thiol-terminated. Examples of thiol-functional polythioethers are disclosed, for example, in U.S. Patent No. 6,172,179. In certain embodiments, a thiol-terminated polythioether comprises Permapol® P3.1E, available from PRC-DeSoto International Inc., Sylmar, CA.

[0068] In certain embodiments, a sulfur-containing polymer comprises a polythioether comprising a backbone comprising the structure of Formula (3):



wherein:

(i) each R^1 is independently selected from a C_{2-10} n-alkanediyl group, a C_{3-6} branched alkanediyl group, a C_{6-8} cycloalkanediyl group, a C_{6-10} alkanecycloalkanediyl group, a heterocyclic group, a $-[(CHR^3)_p-X]_q-(CHR^3)_r$ -group, wherein each R^3 is selected from hydrogen and methyl;

(ii) each R^2 is independently selected from a C_{2-10} n-alkanediyl group, a C_{3-6} branched alkanediyl group, a C_{6-8} cycloalkanediyl group, a C_{6-14} alkanecycloalkanediyl group, a heterocyclic group, and a $-[(CH_2)_p-X]_q-(CH_2)_r$ -group;

(iii) each X is independently selected from O, S, and a -NR- group, in which R is selected from H and a methyl group;

(iv) m ranges from 0 to 50;

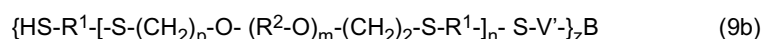
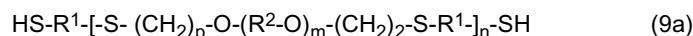
(v) n is an integer ranging from 1 to 60;

(vi) p is an integer ranging from 2 to 6;

(vii) q is an integer ranging from 1 to 5; and

(viii) r is an integer ranging from 2 to 10.

[0069] In certain embodiments, a sulfur-containing polymer comprises a thiol-terminated polythioether selected from a thiol-terminated polythioether of Formula (9a), a thiol-terminated polythioether of Formula (9b), or a combination thereof:



wherein:

each R^1 independently is selected from C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, and $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -, wherein:

s is an integer from 2 to 6;

q is an integer from 1 to 5;

r is an integer from 2 to 10;

each R^3 is independently selected from hydrogen and methyl; and

each X is independently selected from -O-, -S-, and -NR-, wherein

R is selected from hydrogen and methyl;

each R^2 is independently selected from C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, and $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -, wherein s, q, r, R^3 , and X are as defined as for R^1 ;

m is an integer from 0 to 50;

n is an integer from 1 to 60;

p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(-V)_z wherein:

z is an integer from 3 to 6; and

each V is a group comprising a terminal group reactive with thiol groups; and

each -V'- is derived from the reaction of -V with a thiol.

[0070] In certain embodiments, Formula (9a) and in Formula (9b), R^1 is $-[(CH_2)_p-X]_q-(CH_2)_r$ -, where p is 2, X is -O-, q is 2, r is 2, R^2 is ethanediyl, m is 2, and n is 9.

[0071] In certain embodiments of Formula (9a) and Formula (9b), R^1 is selected from C_{2-6} alkanediyl and $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -.

[0072] In certain embodiments of Formula (9a) and Formula (9b), R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -, and in certain embodiments X is -O- and in certain embodiments, X is -S-.

[0073] In certain embodiments of Formula (9a) and Formula (9b), where R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -, p is 2, r is 2, q is 1, and X is -S-; in certain embodiments, wherein p is 2, q is 2, r is 2, and X is -O-; and in certain embodiments, p is 2, r is 2, q is 1, and X is -O-.

[0074] In certain embodiments of Formula (9a) and Formula (9b), where R^1 is $-[(CHR^3)_s-X]_q-(CHR^3)_r$ -, each R^3 is hydrogen, and in certain embodiments, at least one R^3 is methyl.

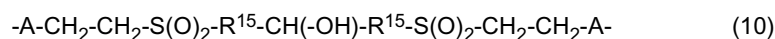
[0075] In certain embodiments of Formula (9a) and Formula (9b), each R^1 is the same, and in certain embodiments, at least one R^1 is different.

[0076] Various methods can be used to prepare such polythioethers. Examples of suitable thiol-functional polythioethers, and methods for their production, are described in U.S. Patent No. 6,172,179 at col. 2, line 29 to col. 4, line

22; col. 6, line 39 to col. 10, line 50; and col. 11, lines 65 to col. 12, line 22. Such thiol-functional polythioethers may be difunctional, that is, linear polymers having two thiol terminal groups, or polyfunctional, that is, branched polymers have three or more thiol terminal groups. Suitable thiol-functional polythioethers are commercially available, for example, as Permapol® P3.1E, from PRC-DeSoto International Inc., Sylmar, CA.

[0077] In certain embodiments, a sulfur-containing polymer comprises a polythioether in which a metal chelating agent such as a bis(sulfonyl)alkanol is incorporated into the polymer backbone. Sulfur-containing polymers in which metal chelating agents are incorporated into the polymer backbone are disclosed in U.S. Application No. 13/923,903, filed on June 21, 2013, and U.S. Application No. (94348-882348 (005110US)).

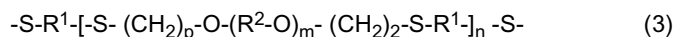
[0078] In certain embodiments, a sulfur-containing polymer comprises a polythioether having the backbone structure of Formula (10):



wherein:

each R^{15} is independently selected from C_{1-3} alkanediyl and substituted C_{1-3} alkanediyl where the one or more substituent groups is -OH;

each A is independently a moiety having the structure of Formula (3):



wherein:

each R^1 independently comprises C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, or $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, wherein:

s is an integer from 2 to 6;

q is an integer from 1 to 5;

r is an integer from 2 to 10;

each R^3 independently comprises hydrogen or methyl; and

each X independently comprises -O-, -S-, and -NR⁵-,

wherein R^5 comprises hydrogen or methyl; and

each R^2 independently comprises C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, or $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, wherein s, q, r, R^3 , and X are as defined for R^1 ;

m is an integer from 0 to 50;

n is an integer from 1 to 60; and

p is an integer from 2 to 6.

[0079] These polythioethers, which contain a bis(sulfonyl)alkanol moiety within the backbone are disclosed in U.S. Application No. 13/923,903 filed on June 21, 2013.

[0080] Suitable thiol-functional polythioethers may be produced by reacting a divinyl ether or mixtures of divinyl ethers with an excess of dithiol or a mixtures of dithiols. For example, dithiols suitable for use in preparing thiol-functional polythioethers include those having Formula (11), other dithiols disclosed herein, or combinations of any of the dithiols disclosed herein.

[0081] In certain embodiments, a dithiol has the structure of Formula (11):



wherein:

R^1 is selected from C_{2-6} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, and $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$; wherein:

each R^3 is independently selected from hydrogen and methyl;

each X is independently selected from -O-, -S-, and -NR- wherein R is selected from hydrogen and methyl;

s is an integer from 2 to 6;

q is an integer from 1 to 5; and

r is an integer from 2 to 10.

[0082] In certain embodiments of a dithiol of Formula (11), R¹ is -[-(CHR³)_s-X]_q-(CHR³)_r.

[0083] In certain embodiments of a compound of Formula (11), X is selected from -O- and -S-, and thus -[-(CHR³)_s-X]_q-(CHR³)_r in Formula (11) is -[-(CHR³)_p-O]_q-(CHR³)_r or -[-(CHR³)₂]_p-S]_q-(CHR³)_r. In certain embodiments, p and r are equal, such as where p and r are both two.

[0084] In certain embodiments of a dithiol of Formula (11), R¹ is selected from C₂₋₆ alkanediyl and -[-(CHR³)_s-X]_q-(CHR³)_r.

[0085] In certain embodiments, R¹ is -[-(CHR³)_s-X]_q-(CHR³)_r, and in certain embodiments X is -O-, and in certain embodiments, X is -S-.

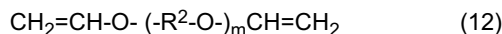
[0086] In certain embodiments where R¹ is -[-(CHR³)_s-X]_q-(CHR³)_r, p is 2, r is 2, q is 1, and X is -S-; in certain embodiments, wherein p is 2, q is 2, r is 2, and X is -O-; and in certain embodiments, p is 2, r is 2, q is 1, and X is -O-.

[0087] In certain embodiments where R¹ is -[-(CHR³)_s-X]_q-(CHR³)_r, each R³ is hydrogen, and in certain embodiments, at least one R³ is methyl.

[0088] Examples of suitable dithiols include, for example, 1,2-ethanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 1,3-butanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,3-pentanedithiol, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,3-dimercapto-3-methylbutane, dipentenedimercaptan, ethylcyclohexyldithiol (ECHDT), dimercaptodiethylsulfide, methyl-substituted dimercaptodiethylsulfide, dimethyl-substituted dimercaptodiethylsulfide, dimercaptodioxaoctane, 1,5-dimercapto-3-oxapentane, and a combination of any of the foregoing. A polythiol may have one or more pendant groups selected from a lower (e.g., C₁₋₆) alkyl group, a lower alkoxy group, and a hydroxyl group. Suitable alkyl pendant groups include, for example, C₁₋₆ linear alkyl, C₃₋₆ branched alkyl, cyclopentyl, and cyclohexyl.

[0089] Other examples of suitable dithiols include dimercaptodiethylsulfide (DMDS) (in Formula (11), R¹ is -[-(CH₂)_p-X]_q-(CH₂)_r, wherein p is 2, r is 2, q is 1, and X is -S-); dimercaptodioxaoctane (DMDO) (in Formula (11), R¹ is -[-(CH₂)_p-X]_q-(CH₂)_r, wherein p is 2, q is 2, r is 2, and X is -O-); and 1,5-dimercapto-3-oxapentane (in Formula (11), R¹ is -[-(CH₂)_p-X]_q-(CH₂)_r, wherein p is 2, r is 2, q is 1, and X is -O-). It is also possible to use dithiols that include both heteroatoms in the carbon backbone and pendant alkyl groups, such as methyl groups. Such compounds include, for example, methyl-substituted DMDS, such as HS-CH₂CH(CH₃)-S-CH₂CH₂-SH, HS-CH(CH₃)CH₂-S-CH₂CH₂-SH and dimethyl substituted DMDS, such as HS-CH₂CH(CH₃)-S-CH(CH₃)CH₂-SH and HS-CH(CH₃)CH₂-S-CH₂CH(CH₃)-SH.

[0090] Suitable divinyl ethers for preparing polythioethers and polythioether adducts include, for example, divinyl ethers of Formula (12):



where R² in Formula (12) is selected from a C₂₋₆ n-alkanediyl group, a C₃₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₆₋₁₀ alkanecycloalkanediyl group, and -[-(CH₂)_p-O]_q-(CH₂)_r, where p is an integer ranging from 2 to 6, q is an integer from 1 to 5, and r is an integer from 2 to 10. In certain embodiments of a divinyl ether of Formula (12), R² is a C₂₋₆ n-alkanediyl group, a C₃₋₆ branched alkanediyl group, a C₆₋₈ cycloalkanediyl group, a C₆₋₁₀ alkanecycloalkanediyl group, and in certain embodiments, -[-(CH₂)_p-O]_q-(CH₂)_r.

[0091] Suitable divinyl ethers include, for example, compounds having at least one oxyalkanediyl group, such as from 1 to 4 oxyalkanediyl groups, i.e., compounds in which m in Formula (12) is an integer ranging from 1 to 4. In certain embodiments, m in Formula (12) is an integer ranging from 2 to 4. It is also possible to employ commercially available divinyl ether mixtures that are characterized by a non-integral average value for the number of oxyalkanediyl units per molecule. Thus, 1 in Formula (12) can also take on rational number values ranging from 0 to 10.0, such as from 1.0 to 10.0, from 1.0 to 4.0, or from 2.0 to 4.0.

[0092] Examples of suitable divinyl ethers include, for example, divinyl ether, ethylene glycol divinyl ether (EG-DVE) (R² in Formula (12) is ethanediyl and m is 1), butanediol divinyl ether (BD-DVE) (R² in Formula (12) is butanediyl and m is 1), hexanediol divinyl ether (HD-DVE) (R² in Formula (12) is hexanediyl and m is 1), diethylene glycol divinyl ether (DEG-DVE) (R² in Formula (12) is ethanediyl and m is 2), triethylene glycol divinyl ether (R² in Formula (12) is ethanediyl and m is 3), tetraethylene glycol divinyl ether (R² in Formula (12) is ethanediyl and m is 4), cyclohexanedimethanol divinyl ether, polytetrahydrofuryl divinyl ether; trivinyl ether monomers, such as trimethylolpropane trivinyl ether; tetrafunctional ether monomers, such as pentaerythritol tetravinyl ether; and combinations of two or more such polyvinyl ether monomers. A polyvinyl ether may have one or more pendant groups selected from alkyl groups, hydroxyl groups, alkoxy groups, and amine groups.

[0093] In certain embodiments, divinyl ethers in which R² in Formula (12) is C₃₋₆ branched alkanediyl may be prepared by reacting a polyhydroxy compound with acetylene. Examples of divinyl ethers of this type include compounds in which R² in Formula (12) is an alkyl-substituted methanediyl group such as -CH(CH₃)- (for example Pluriol® blends such as Pluriol®E-200 divinyl ether (BASF Corp., Parsippany, NJ), for which R² in Formula (12) is ethanediyl and m is 3.8) or an alkyl-substituted ethanediyl (for example -CH₂CH(CH₃)- such as DPE polymeric blends including DPE-2 and DPE-

3 (International Specialty Products, Wayne, NJ)).

[0094] Other useful divinyl ethers include compounds in which R² in Formula (12) is polytetrahydrofuryl (poly-THF) or polyoxyalkanediyl, such as those having an average of about three monomer units.

[0095] Two or more types of polyvinyl ether monomers of Formula (12) may be used. Thus, in certain embodiments, two dithiols of Formula (11) and one polyvinyl ether monomer of Formula (12), one dithiol of Formula (11) and two polyvinyl ether monomers of Formula (12), two dithiols of Formula (11) and two divinyl ether monomers of Formula (12), and more than two compounds of one or both Formula (11) and Formula (12), may be used to produce a variety of thiol-functional polythioethers.

[0096] In certain embodiments, a polyvinyl ether monomer comprises 20 to less than 50 mole percent of the reactants used to prepare a thiol-functional polythioether, and in certain embodiments, 30 to less than 50 mole percent.

[0097] In certain embodiments provided by the present disclosure, relative amounts of dithiols and divinyl ethers are selected to yield polythioethers having terminal thiol groups. Thus, a dithiol of Formula (11) or a mixture of at least two different dithiols of Formula (11), are reacted with of a divinyl ether of Formula (12) or a mixture of at least two different divinyl ethers of Formula (12) in relative amounts such that the molar ratio of thiol groups to vinyl groups is greater than 1:1, such as 1.1 to 2.0:1.0.

[0098] The reaction between compounds of dithiols and divinyl ethers may be catalyzed by a free radical catalyst. Suitable free radical catalysts include, for example, azo compounds, for example azobisnitriles such as azo(bis)isobutyronitrile (AIBN); organic peroxides such as benzoyl peroxide and t-butyl peroxide; and inorganic peroxides such as hydrogen peroxide. The catalyst may be a free-radical catalyst, an ionic catalyst, or ultraviolet radiation. In certain embodiments, the catalyst does not comprise acidic or basic compounds, and does not produce acidic or basic compounds upon decomposition. Examples of free-radical catalysts include azo-type catalyst, such as Vazo®-57 (Du Pont), Vazo®-64 (Du Pont), Vazo®-67 (Du Pont), V-70® (Wako Specialty Chemicals), and V-65B® (Wako Specialty Chemicals). Examples of other free-radical catalysts are alkyl peroxides, such as t-butyl peroxide. The reaction may also be effected by irradiation with ultraviolet light either with or without a cationic photoinitiating moiety.

[0099] Thiol-functional polythioethers provided by the present disclosure may be prepared by combining at least one compound of Formula (11) and at least one compound of Formula (12) followed by addition of an appropriate catalyst, and carrying out the reaction at a temperature from 30 °C to 120 °C, such as 70 °C to 90 °C, for a time from 2 to 24 hours, such as 2 to 6 hours.

[0100] As disclosed herein, thiol-terminated polythioethers may comprise a polyfunctional polythioether, i.e., may have an average functionality of greater than 2.0. Suitable polyfunctional thiol-terminated polythioethers include, for example, those having the structure of Formula (13):



wherein: (i) A comprises, for example, a structure of Formula (3), (ii) B denotes a z-valent residue of a polyfunctionalizing agent; and (iii) z has an average value of greater than 2.0, and, in certain embodiments, a value between 2 and 3, a value between 2 and 4, a value between 3 and 6, and in certain embodiments, is an integer from 3 to 6.

[0101] Polyfunctionalizing agents suitable for use in preparing such polyfunctional thiol-functional polymers include trifunctionalizing agents, that is, compounds where z is 3. Suitable trifunctionalizing agents include, for example, triallyl cyanurate (TAC), 1,2,3-propanetrithiol, isocyanurate-containing trithiols, and combinations thereof, as disclosed in U.S. Publication No. 2010/0010133 at paragraphs [0102]-[0105]. Other useful polyfunctionalizing agents include trimethylolpropane trivinyl ether, and the polythiols described in U.S. Patent. Nos. 4,366,307; 4,609,762; and 5,225,472. Mixtures of polyfunctionalizing agents may also be used.

[0102] As a result, thiol-functional polythioethers suitable for use in embodiments provided by the present disclosure may have a wide range of average functionality. For example, trifunctionalizing agents may afford average functionalities from 2.05 to 3.0, such as from 2.1 to 2.6. Wider ranges of average functionality may be achieved by using tetrafunctional or higher functionality polyfunctionalizing agents. Functionality may also be affected by factors such as stoichiometry, as will be understood by those skilled in the art.

[0103] Thiol-functional polythioethers having a functionality greater than 2.0 may be prepared in a manner similar to the difunctional thiol-functional polythioethers described in U.S. Publication No. 2010/0010133. In certain embodiments, polythioethers may be prepared by combining (i) one or more dithiols described herein, with (ii) one or more divinyl ethers described herein, and (iii) one or more polyfunctionalizing agents. The mixture may then be reacted, optionally in the presence of a suitable catalyst, to afford a thiol-functional polythioether having a functionality greater than 2.0.

[0104] Thus, in certain embodiments, a thiol-terminated polythioether comprises the reaction product of reactants comprising:

(a) a dithiol of Formula (11):



wherein:

R^1 is selected from C_{2-6} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, and $[-(\text{CHR}^3)_s-\text{X}]_q-(\text{CHR}^3)_r$; wherein:

each R^3 is independently selected from hydrogen and methyl;

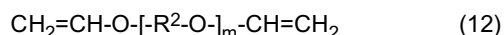
each X is independently selected from -O-, -S-, -NH-, and -NR- wherein R is selected from hydrogen and methyl;

s is an integer from 2 to 6;

q is an integer from 1 to 5; and

r is an integer from 2 to 10; and

(b) a divinyl ether of Formula (12):



wherein:

each R^2 is independently selected from C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, and $[-(\text{CHR}^3)_s-\text{X}]_q-(\text{CHR}^3)_r$, wherein s, q, r, R^3 , and X are as defined above;

m is an integer from 0 to 50;

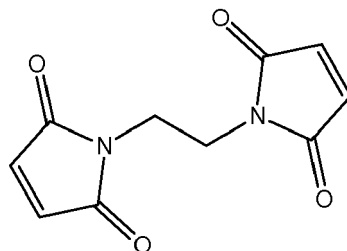
n is an integer from 1 to 60; and

p is an integer from 2 to 6.

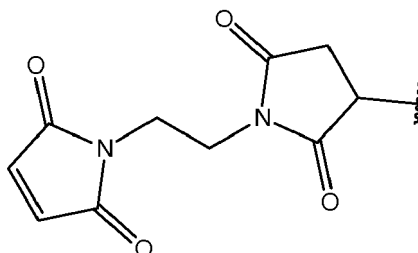
And, in certain embodiments, the reactants comprise (c) a polyfunctional compound such as a polyfunctional compound $\text{B}(-\text{V})_z$, where B, -V, and z are as defined herein.

[0105] Thiol-terminated polythioethers provided by the present disclosure represent thiol-terminated polythioethers having a molecular weight distribution. In certain embodiments, useful thiol-terminated polythioethers can exhibit a number average molecular weight ranging from 500 Daltons to 20,000 Daltons, in certain embodiments, from 2,000 Daltons to 5,000 Daltons, and in certain embodiments, from 3,000 Daltons to 4,000 Daltons. In certain embodiments, useful thiol-terminated polythioethers exhibit a polydispersity (M_w/M_n ; weight average molecular weight/number average molecular weight) ranging from 1 to 20, and in certain embodiments, from 1 to 5. The molecular weight distribution of thiol-terminated polythioethers may be characterized by gel permeation chromatography.

[0106] To prepare sulfur-containing maleimide adduct, a sulfur-containing polymer such as those disclosed herein may be reacted with a compound having a maleimide group and a group that is reactive with the terminal groups of the sulfur-containing polymer. In certain embodiments, a compound having a maleimide group and a group that is reactive with the terminal groups of the sulfur-containing polymer is 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione). In certain embodiments, a compound having a maleimide group and a group that is reactive with the terminal groups of the sulfur-containing polymer is selected from 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione) list the rest. In certain embodiments, each R^6 is derived from ethylenebismaleimide; 1,6-bismaleimido-hexane, 2,4-dimaleimidotoluene; N,N'-1,3-phenylenedimaleimide; 1,4-bis(maleimido)butane; trimethylenebismaleimide; p,p'-dimaleimidodiphenylmethane; pentamethylenebismaleimide 1H-pyrrole-2,5-dione; 1,1'-(1,8-octanediyl)bis-, 1H-pyrrole-2,5-dione, 1,1'-(1,7-heptanediyl)bis-, 4,4'-dithiobis(phenylmaleimide); methylenebis(N-carbamylmaleimide), 1,9-bis(maleimide)nonane; 1,1'-decane-1,10-diylbis(1H-pyrrole-2,5-dione); O-phenylene dimaleimide, bis(N-maleimidomethyl)ether; 1,5-bis(maleimide)-2-methyl-pentane; N,N'-1,4-phenylenedimaleimide; 1,1'-(2-methyl-1,3-phenylene)bis(1H-pyrrole-2,5-dione); Kerimid 601 resin; tetrakis(N-2-aminoethylmaleamide); 1-(2,5-dimethylphenyl)pyrrole-2,5-dione; SureCN331305; SureCN349749; or 1,1'-biphenyl-4,4'-diylbis(1H-pyrrole-2,5-dione). For example, when R^6 is derived from ethylenebismaleimide having the structure:



R⁶ will have the structure:



[0107] The reaction between a sulfur-containing polymer and a compound having a maleimide group and a group that is reactive with a terminal group of the sulfur-containing polymer can be performed in the presence of an appropriate catalyst.

Compositions

[0108] Terminal maleimide groups are Michael acceptors. Michael addition chemistries may be employed in a variety of ways in conjunction with sulfur-containing polymers and sulfur-containing maleimide adducts to provide curable compositions. For example, a curable composition provided by the present disclosure may comprise (a) a sulfur-containing polymer and a maleimide curing agent; (b) a sulfur-containing maleimide adduct and a curing agent comprising at least two terminal groups that are reactive with maleimide groups; or (c) a sulfur-containing polymer and a curing agent comprising a combination of a monomeric maleimide and a sulfur-containing maleimide adduct.

Sulfur-containing polymer and maleimide curing agent

[0109] In certain embodiments, compositions provided by the present disclosure comprise a sulfur-containing polymer and a maleimide curing agent. A sulfur-containing polymer may be a polythioether or combination of polythioethers having terminal groups reactive with the maleimide curing agent; a polysulfide or combination of polysulfides having terminal groups reactive with the maleimide curing agent; a sulfur-containing polyformal or combination of sulfur-containing polyformals having terminal groups reactive with the maleimide curing agent; or a combination of any of the foregoing. In certain embodiments, a sulfur-containing polymer is thiol-terminated. In such embodiments, a maleimide curing agent will be polyfunctional and have maleimide groups reactive with the terminal groups of the sulfur-containing polymer. A maleimide curing agent may be monomeric, may be maleimide-terminated prepolymer adduct such as a maleimide-terminated prepolymer adduct of any of the sulfur-containing polymer disclosed herein, or a combination thereof.

[0110] In certain embodiments, a sulfur-containing polymer comprises a thiol-terminated polythioether, including any of the thiol-terminated polythioethers disclosed herein, such as a thiol-terminated polythioether comprising a backbone of Formula (3), a thiol-terminated polythioether of Formula (9a), a thiol-terminated polythioether of Formula (9b), or a combination of any of the foregoing. In certain embodiments, a sulfur-containing polymer comprises a thiol-terminated polythioether, such as a thiol-terminated polythioether of Formula (9a), Formula (9b), or a combination thereof. In certain embodiments, a sulfur-containing polymer is selected from a difunctional sulfur-containing polymer, a trifunctional-containing polymer, and a combination of thereof. In certain embodiments, a thiol-terminated polymer comprises a mixture of thiol-terminated sulfur-containing polymers having an average functionality from 2 to 3, and in certain embodiments, from 2.2 to 2.8. In certain embodiments, a thiol-terminated polythioether comprises Permapol® 3.1E, available from PRC-DeSoto International.

[0111] A polyfunctional maleimide has at least two maleimide groups. A polyfunctional maleimide may have an average

Michael acceptor functionality from 2 to 6, from 2 to 4, from 2 to 3, and in certain embodiments, from 2.05 to 2.5. In certain embodiments, a polyfunctional maleimide is difunctional, such as 1,1'-(methylenebis(4,1-phenylene)bis(1H-pyrrole-2,5-dione). A maleimide having a functionality greater than two may be prepared by reacting a compound having a maleimide group and a group reactive with terminal groups of a polyfunctionalizing agent such as those disclosed

herein, using appropriate reaction conditions.

[0112] In certain embodiments, a maleimide curing agent is a 1,1' - (methylenebis(4,1-phenylene)bis(1H-pyrrole-2,5-dione). A maleimide curing agent may also include any of the polyfunctional maleimides disclosed herein.

[0113] In certain embodiments where a maleimide is used as a curing agent, the molecular weight of the maleimide curing agent is less than 600 Daltons, less than 400 Daltons, and in certain embodiments, less than 200 Daltons.

[0114] In certain embodiments, a maleimide curing agent comprises from 0.5 wt% to 20 wt% of the composition, from 1 wt % to 10 wt%, from 2 wt% to 8 wt%, from 2 wt% to 6 wt%, and in certain embodiments, from 3 wt% to 5 wt%, where wt% is based on the total dry solids weight of the composition.

[0115] Polyfunctional maleimides may be prepared by reacting a maleimide with a polyfunctionalizing agent. For example, a bismaleimide such as 1,1'-(methylenebis(4,1-phenylene)bis(1H-pyrrole-2,5-dione) may be reacted with a polyfunctionalizing agent having terminal thiol groups to provide a polyfunctional maleimide. Thiol-functional polyfunctionalizing agents are disclosed, for example, in U.S. Application No. 13/529,183, filed on June 21, 2012.

Sulfur-containing maleimide adduct and a curing agent

[0116] In certain embodiments, a composition comprises a sulfur-containing maleimide adduct provided by the present disclosure and a sulfur-containing polymer curing agent. In certain embodiments, a composition comprises a sulfur-containing maleimide adduct provided by the present disclosure, a monomeric maleimide, and a sulfur-containing polymer curing agent. In such compositions a sulfur-containing maleimide adduct comprises any of those disclosed herein. In certain embodiments, a sulfur-containing maleimide adduct comprises a polythioether maleimide adduct, and in certain

embodiments a polythioether maleimide adduct has an average functionality from 2 to 3, from 2.2 to 2.8, and in certain embodiments, from 2.4 to 2.6. In certain embodiments, a sulfur-containing maleimide adduct has an average functionality of 2.

[0117] In certain embodiments, a sulfur-containing maleimide adduct comprises an adduct of Formula (8a), Formula (8b), or a combination thereof, and the sulfur-containing polymer curing agent comprises a polythioether of Formula (9a), Formula (9b), or a combination thereof. In certain embodiments, the sulfur-containing maleimide adduct comprises the maleimide adduct of Permapol® 3.1E. In certain embodiments, the sulfur-containing polymer curing agent comprises Permapol® 3.1E.

[0118] In certain embodiments, a sulfur-containing maleimide adduct comprises an adduct of Formula (8a), Formula (8b), or a combination thereof, and the sulfur-containing polymer curing agent comprises a polysulfide. In certain

embodiments, the sulfur-containing maleimide adduct comprises the maleimide adduct of Permapol® 3.1E. In certain embodiments, the sulfur-containing polymer curing agent comprises a polysulfide selected from a Thiokol-LP® polysulfide, a Thioplast® polysulfide, and a combination thereof.

[0119] In such compositions the maleimide groups of the adduct are reactive with the terminal groups of the sulfur-containing polymer. For example, in certain embodiments the sulfur-containing polymer comprises terminal thiol groups.

[0120] A sulfur-containing polymer used as a curing agent comprises at least two terminal groups reactive with maleimide groups. A sulfur-containing polymer used as a curing agent in such compositions may comprise a polythioether including any of those disclosed herein, a polysulfide including any of those disclosed herein, or a combination thereof. The sulfur-containing polymer may have an average functionality of 2 or any functionality from 2 and 6, such as from 2 to 4, or from 2 to 3.

[0121] In certain embodiments, the sulfur-containing polymer curing agent comprises a thiol-terminated polythioether such as, for example, Permapol® 3.1E. In certain embodiments, the sulfur-containing polymer comprises a thiol-terminated polysulfide such as, for example, a Thiokol-LP® polysulfide, a Thioplast® polysulfide, or a combination thereof.

[0122] In such embodiments, when used as a curing agent, a sulfur-containing polymer, comprises from 20 wt% to 90 wt% of the composition, from 30 wt% to 80 wt%, from 40 wt% to 60 wt%, and in certain embodiments, 50 wt%, where wt% is based on the total dry weight of the composition.

[0123] In such embodiments, a sulfur-containing maleimide adduct comprises from 20 wt% to 90 wt% of the composition, from 30 wt% to 80 wt%, from 40 wt% to 60 wt%, and in certain embodiments, 50 wt%, where wt% is based on the total dry weight of the composition.

[0124] Compositions comprising a sulfur-containing maleimide adduct and a sulfur-containing polymer curing agent may comprise a catalyst such as an amine catalyst including any of those disclosed herein.

[0125] In certain embodiments, a composition comprises a polythioether maleimide adduct and a curing agent. A polythioether adduct includes any of those disclosed herein, such as polythioether maleimide adducts of Formula (8a), Formula (8b), and combinations thereof.

[0126] In certain embodiments of such compositions, the composition comprises a sulfur-containing maleimide adduct provided by the present disclosure and a curing agent selected from a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups, a monomeric thiol, a polythiol, a polyamine, a blocked polyamine, and a combination of any of the foregoing. In certain embodiments, a curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups such as a monomeric thiol, a polythiol, a polyamine, and in certain embodiments, a blocked polyamine. In certain embodiments of such compositions, a curing agent comprises a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups and a compound having at least two terminal groups reactive with maleimide groups selected from a monomeric thiol, a polythiol, a polyamine, a blocked polyamine, a thiol-terminated prepolymer, an amine-terminated prepolymer, and a combination of any of the foregoing.

[0127] In certain embodiments, a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups is selected from a polythioether polymer comprising at least two terminal groups reactive with maleimide groups, a polysulfide polymer comprising at least two terminal groups reactive with maleimide groups, a sulfur-containing polyformal polymer comprising at least two terminal groups reactive with maleimide groups, and a combination thereof. In certain embodiments, the terminal groups reactive with maleimide groups are thiol groups. In such embodiments, a thiol-terminated polythioether may be selected from a polythioether of Formula (9a), a polythioether of Formula (9b), and a combination thereof. In certain embodiments, the sulfur-containing polymer curing agent comprises a thiol-terminated polysulfide such as, for example, Thiokol-LP® and Thioplast® polysulfide polymers.

[0128] In certain compositions, the curing agent comprises a monomeric polythiol. A monomeric polythiol refers to a compound having at least two terminal thiol groups. Examples of monomeric polythiols include dithiols of Formula (11).

Sulfur-containing maleimide adduct, sulfur-containing polymer, and a compound having at least two maleimide groups

[0129] In certain embodiments, a composition comprises a sulfur-containing polymer having terminal groups reactive with maleimides and a sulfur-containing maleimide adduct. In certain embodiments, a composition comprises a sulfur-containing polymer having terminal groups reactive with maleimides, a polyfunctional maleimide, and a sulfur-containing maleimide adduct.

[0130] In such compositions, a sulfur-containing polymer comprises at least two terminal groups reactive with maleimide groups. In such compositions, the sulfur-containing polymer may be selected from a polythioether polymer, a polysulfide polymer, a sulfur-containing polyformal polymer, or a combination thereof, including a suitable polythioether polymer, polysulfide polymer or sulfur-containing polyformal polymer provided by the present disclosure.

[0131] In certain embodiments, a sulfur-containing polymer is selected such that the terminal groups are reactive with the polyfunctional maleimide and with the sulfur-containing maleimide adduct. In certain embodiments, a sulfur-containing polymer comprises terminal thiol groups including any of the thiol-terminated polythioethers, thiol-terminated polysulfides, thiol-terminated sulfur-containing polyformals and combinations of any of the foregoing, as disclosed herein.

[0132] In certain embodiments of such compositions, a sulfur-containing maleimide adduct comprises a polythioether maleimide adduct provided by the present disclosure, a polysulfide maleimide adduct provided by the present disclosure, a sulfur-containing polyformal maleimide adduct provided by the present disclosure, or a combination of any of the foregoing.

[0133] When a composition comprises a polyfunctional monomeric maleimide, any suitable monomeric maleimide having at least two maleimide groups such as, for example, 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione), or other maleimides and combinations thereof, including any of those disclosed herein may be used. In certain embodiments, a composition further comprises one or more polyfunctional Michael acceptors.

[0134] In certain embodiments, a sulfur-containing polymer is selected from a thiol-terminated polythioether of Formula (9a), Formula (9b), and a combination thereof; a polyfunctional maleimide adduct is selected from a polythioether maleimide adduct of Formula (8a), Formula (8b), and a combination thereof; and a polyfunctional monomeric maleimide is selected from a compound having two or more maleimide groups, such as 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione).

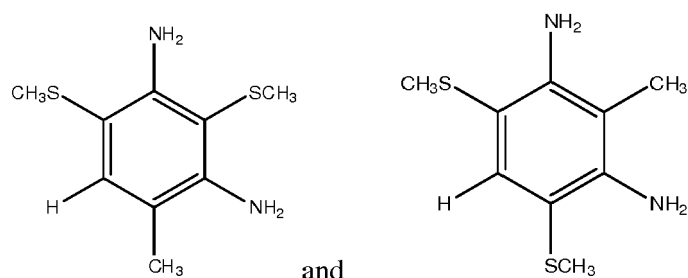
[0135] In such embodiments, the polyfunctional maleimide and sulfur-containing maleimide adduct comprise 10 wt% to 90 wt% of the composition, from 20 wt% to 80 wt%, from 30 wt% to 70 wt%, and in certain embodiments, from 40 wt% to 60 wt%, where wt% is based on the total dry solids weight of the composition.

[0136] Compositions comprising a sulfur-containing polymer, a polyfunctional maleimide, and a sulfur-containing maleimide adduct may comprise a catalyst such as an amine catalyst including polyamine catalysts, including tertiary amine catalysts.

[0137] Examples of polyamines include, for example, aliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines and mixtures thereof. In certain embodiments, the polyamine can include a polyamine having at least two functional groups independently chosen from primary amine (-NH₂), secondary amine (-NH-) and combinations thereof.

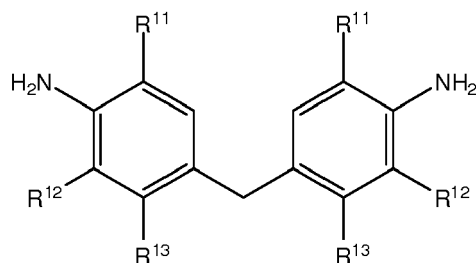
In certain embodiments, the polyamine has at least two primary amine groups.

[0138] In certain embodiments, a polyamine comprises a sulfur-containing polyamine. Examples of suitable sulfur-containing polyamines include isomers of benzenediamine-bis(methylthio)-, such as 1,3-benzenediamine-4-methyl-2,6-bis(methylthio)- and 1,3-benzenediamine-2-methyl-4,6-bis(methylthio)-, having the structure:



[0139] Such sulfur-containing polyamines are commercially available, for example, from Albemarle Corporation under the tradename Ethacure® 300.

[0140] Suitable polyamines also include, for example, polyamines having the following structure:

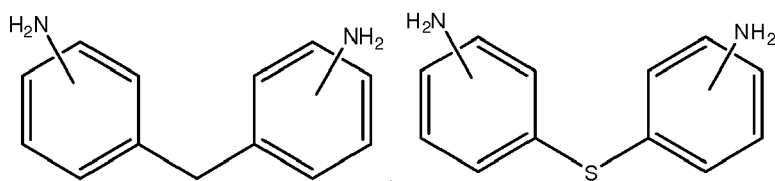


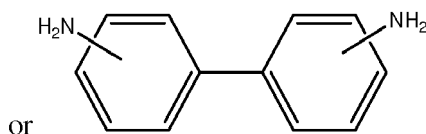
wherein each R^{11} and each R^{12} are independently selected from methyl, ethyl, propyl, and isopropyl groups, and each R^{13} is independently selected from hydrogen and chlorine. Examples of suitable amine-containing curing agents include the following compounds available from Lonza Ltd. (Basel, Switzerland): Lonzacure® M-DIPA, Lonzacure® M-DMA, Lonzacure® M-MEA, Lonzacure® M-DEA, Lonzacure® M-MIPA, Lonzacure® M-CDEA.

[0141] In certain embodiments, a polyamine comprises a diamine, such as 4,4'-methylenebis(3-chloro-2,6-diethyl-aniline) (Lonzacure® M-CDEA), 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene and mixtures thereof (collectively diethyltoluenediamine or DETDA), a sulfur-containing diamine, such as Ethacure® 300, 4,4'-methylene-bis-(2-chloroaniline) and mixtures thereof. Other suitable diamines include 4,4'-methylene-bis(dialkylaniline), 4,4'-methylene-bis(2,6-dimethylaniline), 4,4'-methylene-bis(2,6-diethylaniline), 4,4'-methylene-bis(2-ethyl-6-methylaniline), 4,4'-methylene-bis(2,6-diisopropylaniline), 4,4'-methylene-bis(2-isopropyl-6-methylaniline), 4,4'-methylene-bis(2,6-diethyl-3-chloroaniline), and combinations of any of the foregoing.

[0142] Further, examples of suitable polyamines include ethyleneamines, such as, ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), piperazine, piperidine, substituted piperidine, diethylenediamine (DEDA), 2-amino-1-ethylpiperazine, and combinations thereof. In certain embodiments, a polyamine may be selected from one or more isomers of C_{1-3} dialkyl toluenediamine, such as, 3,5-dimethyl-2,4-toluenediamine, 3,5-dimethyl-2,6-toluenediamine, 3,5-diethyl-2,4-toluenediamine, 3,5-diethyl-2,6-toluenediamine, 3,5-diisopropyl-2,4-toluenediamine, 3,5-diisopropyl-2,6-toluenediamine, and combinations thereof. In certain embodiments, a polyamine may be selected from methylene dianiline, trimethyleneglycol di(para-aminobenzoate), and combinations thereof.

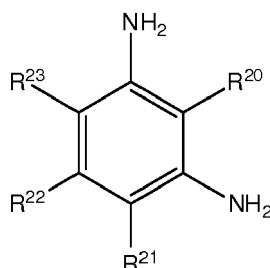
[0143] In certain embodiments, a polyamine includes a compound having the structure:





[0144] In certain embodiments, a polyamine includes one or more methylene bis anilines, one or more aniline sulfides, and/or one or more bianilines which can be represented by the general structures disclosed, for example, in paragraph [0072] of U.S. Publication No. 2011/0092639.

[0145] In certain embodiments, a polyamine includes compounds represented by the general structure:



where R^{20} , R^{21} , R^{22} , and R^{23} are independently selected from C_{1-3} alkyl, CH_3-S- and halogen, such as but not limited to chlorine or bromine. In certain embodiments, a polyamine represented by the immediately preceding structure can be diethyl toluene diamine (DETDA) wherein R^{23} is methyl, R^{20} and R^{21} are each ethyl, and R^{22} is hydrogen. In certain

embodiments, the polyamine is 4,4'-methylenedianiline.

[0146] Examples of blocked polyamines include ketimines, enamines, oxazolidines, aldimines, and imidazolidines. In certain embodiments, the blocked polyamine is Vestamin® A 139 (Evonik).

[0147] Suitable polyamines also include amine-terminated sulfur-containing polyformal adducts, amine-terminated polysulfide adducts, and/or amine-terminated polythioether adducts. Amine-terminated prepolymer adducts such as adducts of polythioethers, polysulfides, or sulfur-containing polyformals may be prepared, for example, by reacting an activated alkenyl-terminated or Michael acceptor-terminated prepolymer with an amino-substituted aniline such as 4-(aminomethyl)aniline, an alkylamine or any other diamine such as n-butylamine, optionally in the presence of a catalyst such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in an organic solvent to provide the corresponding amine-terminated prepolymer. Alternatively, amine-terminated sulfur-containing prepolymers may be obtained by reacting an isocyanate-terminated prepolymer with a diamine such as 4-(aminomethyl)aniline to provide the corresponding amine-terminated prepolymer. Amine-terminated prepolymers may also be obtained by reacting a hydroxyl-terminated prepolymer with an amino-substituted benzoate such as ethyl-4-aminobenzoate in the presence of Bu_2SnO or NaOMe at elevated temperature to provide the corresponding amine-terminated prepolymer.

Epoxy blend

[0148] In certain embodiments, compositions provided by the present disclosure comprise an epoxy curing agent. Thus, in addition to a maleimide curing agent, a sulfur-containing polymer curing agent, and/or a sulfur-containing maleimide adduct curing agent, a composition may comprise one or more polyepoxy curing agents. Examples of suitable epoxies include, for example, polyepoxide resins such as hydantoin diepoxide, diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-F, Novolac® type epoxides such as DEN™ 438 (available from Dow), certain epoxidized unsaturated resins, and combinations of any of the foregoing. A polyepoxide refers to a compound having two or more reactive epoxy groups.

[0149] In certain embodiments, a polyepoxy curing agent comprises an epoxy-functional polymer. Examples of suitable epoxy-functional polymers include the epoxy-functional sulfur-containing polyformal polymers disclosed in U.S. Publication No. 2012/0238707 and epoxy-functional polythioether polymers disclosed in U.S. Patent No. 7,671,145. In general, when used as a curing agent, an epoxy-functional polymer has a molecular weight less than 2,000 Daltons, less than 1,500, Daltons, less than 1,000 Daltons, and in certain embodiments, less than 500 Daltons. Epoxy-functional sulfur-containing polymers may be formed, for example, by reacting a thiol-functional sulfur-containing polymer with a diepoxide or with an epoxy olefin.

[0150] In such compositions, an epoxy curing agent may comprise 0.5 wt% to 20 wt% of the composition, from 1 wt% to 10 wt%, from 2 wt% to 8 wt%, from 2 wt% to 6 wt%, and in certain embodiments, from 3 wt% to 5 wt%, where wt% is based on the total solids weight of the composition.

Isocyanate blend

[0151] In certain embodiments, compositions provided by the present disclosure comprise an isocyanate curing agent. Thus, in addition to a maleimide curing agent, a sulfur-containing polymer curing agent, and/or a sulfur-containing maleimide adduct curing agent, a composition may comprise one or more polyisocyanate curing agents that are reactive with thiol groups but not reactive with maleimide groups. Examples of suitable isocyanate curing agents include toluene diisocyanate, and combinations of any of the foregoing. Isocyanate curing agents are commercially available and include, for example, products under the tradenames Baydur® (Bayer MaterialScience), Desmodur® (Bayer MaterialScience), Solubond® (DSM), ECCO (ECCO), Vestanat® (Evonik), Irodur® (Huntsman), Rhodocoat™ (Perstorp), and Vanchem® (V.T. Vanderbilt). In certain embodiments, an isocyanate curing agent comprises an isocyanate-functional polymer. Examples of suitable isocyanate-functional polymers include the isocyanate-functional sulfur-containing polyformal polymers disclosed in U.S. Publication No. 2012/0238708. In general, when used as a curing agent, an isocyanate-functional polymer has a molecular weight less than 2,000 Daltons, less than 1,500, Daltons, less than 1,000 Daltons, and in certain embodiments, less than 500 Daltons.

[0152] In certain embodiments, suitable diisocyanates include TDI, Isonate™ 143L (polycarbodiimide-modified diphenylmethane diisocyanate), Desmodur® N3400 (1,3-diazetidino-2,4-dione, 1,3-bis(6-isocyanatohexyl)-), IPDI (isophorone diisocyanate), and/or Desmodur® W (H₁₂MDI).

[0153] Examples of suitable aliphatic diisocyanates include, 1,6-hexamethylene diisocyanate, 1,5-diisocyanato-2-methylpentane, methyl-2,6-diisocyanatohexanoate, bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 2,2,4-trimethylhexane 1,6-diisocyanate, 2,4,4-trimethylhexane 1,6-diisocyanate, 2,5(6)-bis(isocyanatomethyl)cyclo[2.2.1]heptane, 1,3,3-trimethyl-1-(isocyanatomethyl)-5-isocyanatocyclohexane, 1,8-diisocyanato-2,4-dimethyloctane, octahydro-4,7-methano-1H-indenedimethyl diisocyanate, and 1,1'-methylenebis(4-isocyanatocyclohexane), and 4,4'-methylene dicyclohexyl diisocyanate (H₁₂MDI). Examples of aromatic diisocyanates include 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate (2,6-TDI), 2,4-toluene diisocyanate (2,4-TDI), a blend of 2,4-TDI and 2,6-TDI, 1,5-diisocyanatonaphthalene, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate (4,4'-MDI), 2,4'-methylenediphenyl diisocyanate (2,4'-MDI), 2,2'-diisocyanatodiphenylmethane (2,2'-MDI), diphenylmethane diisocyanate (MDI), 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl benzene, and 2,4,6-triisopropyl-m-phenylene diisocyanate.

[0154] Examples of suitable aromatic diisocyanates in which the isocyanate groups are not bonded directly to the aromatic ring include, bis(isocyanatoethyl)benzene, α , α , α' , α' -tetramethylxylene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl)phthalate, and 2,5-di(isocyanatomethyl)furan. Aromatic diisocyanates having isocyanate groups bonded directly to the aromatic ring include phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, diphenylether diisocyanate, bis(isocyanatophenylether)ethyleneglycol, bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate, dichlorocarbazole diisocyanate, 4,4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, 2,4-toluene diisocyanate, and 2,6-toluene diisocyanate.

[0155] Examples of suitable alicyclic diisocyanates include isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane.

[0156] In such compositions, an isocyanate curing agent may comprise 0.5 wt% to 20 wt% of the composition, from 1 wt % to 10 wt%, from 2 wt% to 8 wt%, from 2 wt% to 6 wt%, and in certain embodiments, from 3 wt% to 5 wt% of the composition, where wt% is based on the total solids weight of the composition.

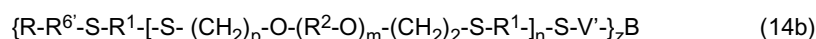
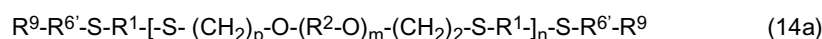
Hydroxyl and amine curing

[0157] Sulfur-containing maleimide adducts provided by the present disclosure may also be modified for use in particular applications and curing chemistries. For example, spray seal applications require rapid curing without heating.

Amine-based systems using epoxy curing agents are well suited for such applications. Accordingly, sulfur-containing maleimide adducts may be adapted to other curing chemistries by modifying or capping the terminal maleimide groups with, for example, hydroxyl groups or amine groups.

[0158] Hydroxyl-terminated sulfur-containing maleimide adducts may be prepared by reacting a sulfur-containing maleimide adduct provided by the present disclosure such as an adduct of Formula (8a) or Formula (8b) with a compound having a terminal thiol group and a terminal hydroxyl group. In certain embodiments, a compound having a terminal thiol group and a terminal hydroxyl group has the structure HS-R¹¹-OH, where R¹¹ is selected from C₂₋₆ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₀ alkanecycloalkanediyl, C₅₋₈ heterocycloalkanediyl, C₆₋₈ arenediyl, C₆₋₁₀ alkanearenediyl, C₅₋₈ heteroarenediyl, and $\square[\square(\text{CHR}^3)_s \square \text{X} \square]_q \square(\text{CHR}^3)_r \square$, where q, r, s, X, and R³ are defined as for Formula (21). In certain embodiments, a sulfur-containing maleimide adduct is derived from Permapol® 3.1E. The reaction may take place in the presence of a catalyst at a temperature from 25 °C to 50 °C.

[0159] In certain embodiments, a hydroxyl-terminated sulfur-containing maleimide adduct comprises a hydroxyl-terminated polythioether maleimide adduct of Formula (14a), a hydroxyl-terminated polythioether maleimide adduct of Formula (14b), or a combination thereof:



wherein:

each R¹ independently is selected from C₂₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₀ alkanecycloalkanediyl, C₅₋₈ heterocycloalkanediyl, and $\text{-}[(\text{-CHR}^3\text{-})_s\text{-X-}]_q\text{-}(\text{-CHR}^3\text{-})_r\text{-}$, wherein:

s is an integer from 2 to 6;

q is an integer from 1 to 5;

r is an integer from 2 to 10;

each R³ is independently selected from hydrogen and methyl; and

each X is independently selected from -O-, -S-, and -NR-, wherein

R is selected from hydrogen and methyl;

each R² is independently selected from C₁₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₄ alkanecycloalkanediyl, and $\text{-}[(\text{-CHR}^3\text{-})_s\text{-X-}]_q\text{-}(\text{-CHR}^3\text{-})_r\text{-}$, wherein s, q, r, R³, and X are as defined for R¹;

m is an integer from 0 to 50;

n is an integer from 1 to 60;

p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(-V)_z wherein:

z is an integer from 3 to 6; and

each V is a group comprising a terminal group reactive with thiol groups;

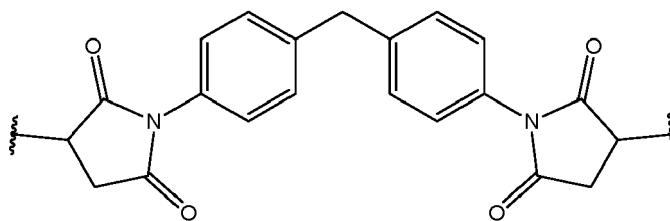
each -V'- is derived from the reaction of -V with a thiol;

each -R^{6'}- is a group derived from a compound having a terminal maleimide group and a group reactive with a thiol group; and

each R⁹- is a moiety having a terminal hydroxyl group.

[0160] In certain embodiments of Formula (14a) and Formula (14b), each R⁹ is -S-R¹¹-OH, wherein R¹¹ is defined herein.

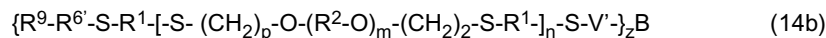
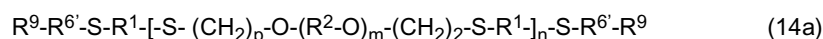
[0161] In certain embodiments of hydroxyl-terminated sulfur-containing maleimide adducts of Formula (14a) and Formula (14b), each R^{6'} is derived from a bismaleimide, such as 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione). Thus, in certain embodiments, R^{6'} has the structure:



[0162] In certain embodiments, compositions comprise one or more hydroxyl-terminated sulfur-containing maleimide adducts and one or more polyisocyanate curing agents. Examples of suitable isocyanate curing agents include toluene diisocyanate, and combinations of any of the foregoing. Isocyanate curing agents are commercially available and include, for example, products under the tradenames Baydur® (Bayer MaterialScience), Desmodur® (Bayer MaterialScience), Solubond® (DSM), ECCO (ECCO), Vestanat® (Evonik), Irodur® (Huntsman), Rhodocoat™ (Perstorp), and Vanchem® (V.T. Vanderbilt).

[0163] Amine-terminated sulfur-containing maleimide adducts may be prepared by reacting a sulfur-containing maleimide adduct provided by the present disclosure such as an adduct of Formula (8a) or Formula (8b) with a compound having a terminal thiol group and a terminal amine group. In certain embodiments, a compound having a terminal thiol group and a terminal amine group has the structure HS-R¹¹-N(R¹²)H, where R¹¹ is selected from C₂₋₆ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₀ alkanecycloalkanediyl, C₅₋₈ heterocycloalkanediyl, C₆₋₈ arenediyl, C₆₋₁₀ alkanearenenediyl, C₅₋₈ heteroarenenediyl, and $\square[\square(\text{CHR}^3)_s\square\text{X}\square]_q\square(\text{CHR}^3)_r\square$, where q, r, s, X, and R³ are defined as for Formula (11). In certain embodiments, R¹² is selected from hydrogen and C₁₋₃ alkyl, and in certain embodiments, R¹² is hydrogen. In certain embodiments, an amine-terminated sulfur-containing maleimide adduct is derived from Permapol® 3.1E, a thiol-terminated polythioether blend. The reaction may take place in the presence of a catalyst at a temperature from 25 °C to 50 °C.

[0164] In certain embodiments, an amine-terminated sulfur-containing maleimide adduct comprises an amine-terminated polythioether adduct of Formula (14a), an amine-terminated polythioether adduct of Formula (14b), or a combination thereof:



wherein:

each R¹ independently is selected from C₂₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₀ alkanecycloalkanediyl, C₅₋₈ heterocycloalkanediyl, and $\text{--}[(\text{--CHR}^3\text{--})_s\text{--X--}]_q\text{--}(\text{--CHR}^3\text{--})_r\text{--}$, wherein:

s is an integer from 2 to 6;

q is an integer from 1 to 5;

r is an integer from 2 to 10;

each R³ is independently selected from hydrogen and methyl; and

each X is independently selected from --O--, --S--, and --NR--, wherein

R is selected from hydrogen and methyl;

each R² is independently selected from C₁₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₄ alkanecycloalkanediyl, and $\text{--}[(\text{--CHR}^3\text{--})_s\text{--X--}]_q\text{--}(\text{--CHR}^3\text{--})_r\text{--}$, wherein s, q, r, R³, and X are as defined for R¹;

m is an integer from 0 to 50;

n is an integer from 1 to 60;

p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(-V)_z wherein:

z is an integer from 3 to 6; and

each V is a group comprising a terminal group reactive with thiol groups;

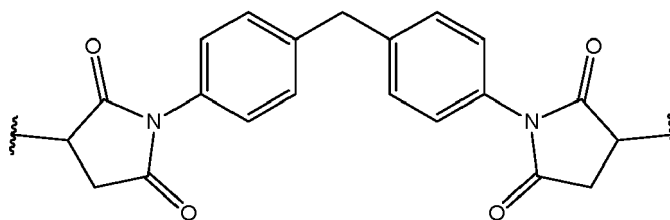
each -V' is derived from the reaction of -V with a thiol;

each -R^{6'}- is a group derived from a compound having a terminal maleimide group and a group reactive with a thiol group; and

each R⁹- is a moiety having a terminal amine group.

[0165] In certain embodiments, R^9 is $-S-R^{11}-N(R^{12})H$, and in certain embodiments of Formula (14a) and Formula (14b), R^9 is $-S-R^{11}-NH_2$.

[0166] In certain embodiments of amine-terminated sulfur-containing maleimide adducts of Formula (14a) and Formula (14b), each R^6 is derived from a bismaleimide, such as 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione). Thus, in certain embodiments, R^6 has the structure:



In certain embodiments, compositions comprise one or more amine-terminated sulfur-containing maleimide adducts and one or more polyisocyanate curing agents such as any of those disclosed herein.

Additional Components

[0167] Compositions provided by the present disclosure may include one or more catalysts. Catalysts appropriate for use in reactions between Michael acceptors such as activated alkenyl groups and thiol groups include basic catalysts such as amines, and in particular, tertiary amines. Examples of suitable amine catalysts include, for example, triethylenediamine (1,4-diazabicyclo[2.2.2]octane, DABCO), dimethylcyclohexylamine (DMCHA), dimethylethanolamine (DMEA), bis-(2-dimethylaminoethyl)ether, N-ethylmorpholine, triethylamine, 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), pentamethyldiethylenetriamine (PMDETA), benzyldimethylamine (BDMA), N,N,N'-trimethyl-N'-hydroxyethyl-bis(aminoethyl)ether, and N'-(3-(dimethylamino)propyl)-N,N-dimethyl-1,3-propanediamine.

[0168] In compositions comprising epoxies, the composition may comprise a basic catalyst, including amine catalysts such as any of those disclosed herein.

[0169] In certain embodiments, compositions provided by the present disclosure comprise one or more adhesion promoters. An adhesion promoter may be present in amount from 0.1 wt% to 15 wt% of a composition, less than 5 wt%, less than 2 wt%, and in certain embodiments, less than 1 wt%, based on the total dry weight of the composition. Examples of adhesion promoters include phenolics, such as Methylon® phenolic resin, and organosilanes, such as epoxy, mercapto or amino functional silanes, such as Silquest® A-187 and Silquest® A-1100. Other useful adhesion promoters are known in the art.

[0170] Compositions provided by the present disclosure may comprise one or more different types of filler. Suitable fillers include those commonly known in the art, including inorganic fillers, such as carbon black and calcium carbonate ($CaCO_3$), silica, polymer powders, and lightweight fillers. Suitable lightweight fillers include, for example, those described in U.S. Patent No. 6,525,168. In certain embodiments, a composition includes 5 wt% to 60 wt% of the filler or combination of fillers, 10 wt% to 50 wt%, and in certain embodiments, from 20 wt% to 40 wt%, based on the total dry weight of the composition. Compositions provided by the present disclosure may further include one or more colorants, thixotropic agents, accelerators, fire retardants, adhesion promoters, solvents, masking agents, or a combination of any of the foregoing. As can be appreciated, fillers and additives employed in a composition may be selected so as to be compatible with each other as well as the polymeric component, curing agent, and or catalyst.

[0171] In certain embodiments, compositions provided by the present disclosure comprise at least one filler that is effective in reducing the specific gravity of the composition. In certain embodiments, the specific gravity of a composition is from 0.8 to 1.0, 0.7 to 0.9, from 0.75 to 0.85, and in certain embodiments, is 0.8. In certain embodiments, the specific gravity of a composition is less than 0.9, less than 0.8, less than 0.75, less than 0.7, less than 0.65, less than 0.6, and in certain embodiments, less than 0.55.

[0172] In certain embodiments, compositions provided by the present disclosure include low density filler particles. As used herein, low density, when used with reference to such particles means that the particles have a specific gravity of no more than 0.7, in certain embodiments no more than 0.25, and in certain embodiments, no more than 0.1. Suitable lightweight filler particles often fall within two categories - microspheres and amorphous particles. The specific gravity of microspheres may range from 0.1 to 0.7 and include, for example, polystyrene foam, microspheres of polyacrylates and polyolefins, and silica microspheres having particle sizes ranging from 5 to 100 microns and a specific gravity of 0.25 (Eccospheres®). Other examples include alumina/silica microspheres having particle sizes in the range of 5 to 300 microns and a specific gravity of 0.7 (Fillite®), aluminum silicate microspheres having a specific gravity of from 0.45 to 0.7 (Z-Light®), calcium carbonate-coated polyvinylidene copolymer microspheres having a specific gravity of 0.13 (Du-

alite® 6001AE), and calcium carbonate coated acrylonitrile copolymer microspheres such as Dualite® E135, having an average particle size of 40 μm and a density of 0.135 g/cc (Henkel). Suitable fillers for decreasing the specific gravity of the composition include, for example, hollow microspheres such as Expancel® microspheres (available from AkzoNobel) or Dualite® low density polymer microspheres (available from Henkel). In certain embodiments, compositions provided by the present disclosure include lightweight filler particles comprising an exterior surface coated with a thin coating, such as those described in U.S. Publication No. 2010/0041839 at paragraphs [0016]-[0052].

[0173] In certain embodiments, a low density filler comprises less than 2 wt% of a composition, less than 1.5 wt%, less than 1.0 wt%, less than 0.8 wt%, less than 0.75 wt%, less than 0.7 wt% and in certain embodiments, less than 0.5 wt% of a composition, where wt% is based on the total dry solids weight of the composition.

[0174] In certain embodiments, compositions provided by the present disclosure comprise an electrically conductive filler. Electrical conductivity and EMI/RFI shielding effectiveness can be imparted to composition by incorporating conductive materials within the polymer. The conductive elements can include, for example, metal or metal-plated particles, fabrics, meshes, fibers, and combinations thereof. The metal can be in the form of, for example, filaments, particles, flakes, or spheres. Examples of metals include copper, nickel, silver, aluminum, tin, and steel. Other conductive materials that can be used to impart EMI/RFI shielding effectiveness to polymer compositions include conductive particles or fibers comprising carbon or graphite. Conductive polymers such as polythiophenes, polypyrroles, polyaniline, poly(p-phenylene) vinylene, polyphenylene sulfide, polyphenylene, and polyacetylene can also be used.

[0175] Electrically conductive fillers also include high band gap materials such as zinc sulfide and inorganic barium compounds.

[0176] Other examples of electrically conductive fillers include electrically conductive noble metal-based fillers such as pure silver; noble metal-plated noble metals such as silver-plated gold; noble metal-plated non-noble metals such as silver plated copper, nickel or aluminum, for example, silver-plated aluminum core particles or platinum-plated copper particles; noble-metal plated glass, plastic or ceramics such as silver-plated glass microspheres, noble-metal plated aluminum or noble-metal plated plastic microspheres; noble-metal plated mica; and other such noble-metal conductive fillers. Non-noble metal-based materials can also be used and include, for example, non-noble metal-plated non-noble metals such as copper-coated iron particles or nickel plated copper; non-noble metals, e.g., copper, aluminum, nickel, cobalt; non-noble-metal-plated-non-metals, e.g., nickel-plated graphite and non-metal materials such as carbon black and graphite. Combinations of electrically conductive fillers can also be used to meet the desired conductivity, EMI/RFI shielding effectiveness, hardness, and other properties suitable for a particular application.

[0177] The shape and size of the electrically conductive fillers used in the compositions of the present disclosure can be any appropriate shape and size to impart electrical conductivity and/or EMI/RFI shielding effectiveness to the cured composition. For example, fillers can be of any shape that is generally used in the manufacture of electrically conductive fillers, including spherical, flake, platelet, particle, powder, irregular, fiber, and the like. In certain sealant compositions of the disclosure, a base composition can comprise Ni-coated graphite as a particle, powder or flake. In certain embodiments, the amount of Ni-coated graphite in a base composition can range from 40 wt% to 80 wt%, and in certain embodiments can range from 50 wt% to 70 wt%, based on the total weight of the base composition. In certain embodiments, an electrically conductive filler can comprise Ni fiber. Ni fiber can have a diameter ranging from 10 μm to 50 μm and have a length ranging from 250 μm to 750 μm . A base composition can comprise, for example, an amount of Ni fiber ranging from 2 wt% to 10 wt%, and in certain embodiments, from 4 wt% to 8 wt%, based on the total weight of the base composition.

[0178] Carbon fibers, particularly graphitized carbon fibers, can also be used to impart electrical conductivity to compositions of the present disclosure. Carbon fibers formed by vapor phase pyrolysis methods and graphitized by heat treatment and which are hollow or solid with a fiber diameter ranging from 0.1 micron to several microns, have high electrical conductivity. As disclosed in U.S. Patent No. 6,184,280, carbon microfibers, nanotubes or carbon fibrils having an outer diameter of less than 0.1 μm to tens of nanometers can be used as electrically conductive fillers. An example of graphitized carbon fiber suitable for conductive compositions of the present disclosure include Panex® 30MF (Zoltek Companies, Inc., St. Louis, Mo.), a 0.921 μm diameter round fiber having an electrical resistivity of 0.00055 $\Omega\text{-cm}$.

[0179] The average particle size of an electrically conductive filler can be within a range useful for imparting electrical conductivity to a polymer-based composition. For example, in certain embodiments, the particle size of the one or more fillers can range from 0.25 μm to 250 μm , in certain embodiments can range from 0.25 μm to 75 μm , and in certain embodiments can range from 0.25 μm to 60 μm . In certain embodiments, composition of the present disclosure can comprise Ketjen Black EC-600 JD (Akzo Nobel, Inc., Chicago, Ill.), an electrically conductive carbon black characterized by an iodine absorption of 1000-11500 mg/g (J0/84-5 test method), and a pore volume of 480-510 $\text{cm}^3/100\text{ gm}$ (DBP absorption, KTM 81-3504). In certain embodiments, an electrically conductive carbon black filler is Black Pearls 2000 (Cabot Corporation, Boston, Mass.).

[0180] In certain embodiments, electrically conductive polymers can be used to impart or modify the electrical conductivity of compositions of the present disclosure. Polymers having sulfur atoms incorporated into aromatic groups or adjacent to double bonds, such as in polyphenylene sulfide, and polythiophene, are known to be electrically conductive.

Other electrically conductive polymers include, for example, polypyrroles, polyaniline, poly(p-phenylene) vinylene, and polyacetylene. In certain embodiments, the sulfur-containing polymers forming a base composition can be polysulfides, sulfur-containing polyformals, and/or polythioethers. As such, the sulfur-containing polymers can comprise aromatic sulfur groups and sulfur atoms adjacent to conjugated double bonds to enhance the electrical conductivity of the compositions of the present disclosure.

[0181] Compositions of the present disclosure can comprise more than one electrically conductive filler and the more than one electrically conductive filler can be of the same or different materials and/or shapes. For example, a sealant composition can comprise electrically conductive Ni fibers, and electrically conductive Ni-coated graphite in the form of powder, particles or flakes. The amount and type of electrically conductive filler can be selected to produce a sealant composition which, when cured, exhibits a sheet resistance (four-point resistance) of less than $0.50 \Omega/\text{cm}^2$, and in certain embodiments, a sheet resistance less than $0.15 \Omega/\text{cm}^2$. The amount and type of filler can also be selected to provide effective EMI/RFI shielding over a frequency range of from 1 MHz to 18 GHz for an aperture sealed using a sealant composition of the present disclosure.

[0182] In certain embodiments, an electrically conductive base composition can comprise an amount of electrically non-conductive filler ranging from 2 wt% to 10 wt% based on the total weight of the base composition, and in certain embodiments, can range from 3 wt% to 7 wt%. In certain embodiments, a curing agent composition can comprise an amount of electrically non-conductive filler ranging from less than 6 wt% and in certain embodiments ranging from 0.5% to 4% by weight, based on the total weight of the curing agent composition.

[0183] Galvanic corrosion of dissimilar metal surfaces and the conductive compositions of the present disclosure can be minimized or prevented by adding corrosion inhibitors to the composition, and/or by selecting appropriate conductive fillers. In certain embodiments, corrosion inhibitors include strontium chromate, calcium chromate, magnesium chromate, and combinations thereof. U.S. Patent No. 5,284,888 and U.S. Patent No. 5,270,364 disclose the use of aromatic triazoles to inhibit corrosion of aluminum and steel surfaces. In certain embodiments, a sacrificial oxygen scavenger such as Zn can be used as a corrosion inhibitor. In certain embodiments, the corrosion inhibitor can comprise less than 10% by weight of the total weight of the electrically conductive composition. In certain embodiments, the corrosion inhibitor can comprise an amount ranging from 2% by weight to 8% by weight of the total weight of the electrically conductive composition. Corrosion between dissimilar metal surfaces can also be minimized or prevented by the selection of the type, amount, and properties of the conductive fillers comprising the composition.

[0184] In certain embodiments, a sulfur-containing polymer and/or sulfur-containing polymer Michael acceptor adduct comprises from 50 wt% to 90 wt% of a composition, from 60 wt% to 90 wt%, from 70 wt% to 90 wt%, and in certain embodiments, from 80 wt% to 90 wt% of the composition, where wt% is based on the total dry solids weight of the composition.

[0185] A composition may also include any number of additives as desired. Examples of suitable additives include plasticizers, pigments, surfactants, adhesion promoters, thixotropic agents, fire retardants, masking agents, and accelerators (such as amines, including 1,4-diazabicyclo[2.2.2] octane, DABCO®), and combinations of any of the foregoing. When used, the additives may be present in a composition in an amount ranging, for example, from 0% to 60% by weight. In certain embodiments, additives may be present in a composition in an amount ranging from 25% to 60% by weight.

Uses

[0186] Compositions provided by the present disclosure may be used, for example, in sealants, coatings, encapsulants, and potting compositions. A sealant includes a composition capable of producing a film that has the ability to resist operational conditions, such as moisture and temperature, and at least partially block the transmission of materials, such as water, fuel, and other liquid and gases. A coating composition includes a covering that is applied to the surface of a substrate to, for example, improve the properties of the substrate such as the appearance, adhesion, wettability, corrosion resistance, wear resistance, fuel resistance, and/or abrasion resistance. A potting composition includes a material useful in an electronic assembly to provide resistance to shock and vibration and to exclude moisture and corrosive agents. In certain embodiments, sealant compositions provided by the present disclosure are useful, e.g., as aerospace sealants and as linings for fuel tanks.

[0187] In certain embodiments, compositions, such as sealants, may be provided as multi-pack compositions, such as two-pack compositions, wherein one package comprises one or more thiol-terminated polythioethers provided by the present disclosure and a second package comprises one or more polyfunctional sulfur-containing epoxies provided by the present disclosure. Additives and/or other materials may be added to either package as desired or necessary. The two packages may be combined and mixed prior to use. In certain embodiments, the pot life of the one or more mixed thiol-terminated polythioethers and epoxies is at least 30 minutes, at least 1 hour, at least 2 hours, and in certain embodiments, more than 2 hours, where pot life refers to the period of time the mixed composition remains suitable for use as a sealant after mixing.

[0188] Compositions, including sealants, provided by the present disclosure may be applied to any of a variety of substrates. Examples of substrates to which a composition may be applied include metals such as titanium, stainless steel, and aluminum, any of which may be anodized, primed, organic-coated or chromate-coated; epoxy; urethane; graphite; fiberglass composite; Kevlar®; acrylics; and polycarbonates. In certain embodiments, compositions provided

by the present disclosure may be applied to a coating on a substrate, such as a polyurethane coating.

[0189] Compositions provided by the present disclosure may be applied directly onto the surface of a substrate or over an underlayer by any suitable coating process known to those of ordinary skill in the art.

[0190] Furthermore, methods are provided for sealing an aperture utilizing a composition provided by the present disclosure. These methods comprise, for example, applying a composition provided by the present disclosure to a surface to seal an aperture, and curing the composition. In certain embodiments, a method for sealing an aperture comprises (a) applying a sealant composition provided by the present disclosure to one or more surfaces defining an aperture, (b) assembling the surfaces defining the aperture, and (c) curing the sealant, to provide a sealed aperture. In certain embodiments, a method of sealing an aperture comprises (a) applying a sealant composition provided by the present disclosure to one or more surfaces defining an aperture, and (b) curing the sealant, to provide a sealed aperture.

[0191] In certain embodiments, a composition may be cured under ambient conditions, where ambient conditions refers to a temperature from 20 °C to 25 °C, and atmospheric humidity. In certain embodiments, a composition may be cured under conditions encompassing a temperature from a 0 °C to 100 °C and humidity from 0% relative humidity to 100% relative humidity. In certain embodiments, a composition may be cured at a higher temperature such as at least 30 °C, at least 40 °C, and in certain embodiments, at least 50 °C. In certain embodiments, a composition may be cured at room temperature, e.g., 25 °C. In certain embodiments, a composition may be cured upon exposure to actinic radiation, such as ultraviolet radiation. As will also be appreciated, the methods may be used to seal apertures on aerospace vehicles including aircraft and aerospace vehicles.

[0192] In certain embodiments, the composition achieves a tack-free cure in less than 2 hours, less than 4 hours, less than 6 hours, less than 8 hours, and in certain embodiments, less than 10 hours, at a temperature of less than 93°C (200 °F).

[0193] The time to form a viable seal using curable compositions of the present disclosure can depend on several factors as can be appreciated by those skilled in the art, and as defined by the requirements of applicable standards and specifications. In general, curable compositions of the present disclosure develop adhesion strength within 24 hours to 30 hours, and 90% of full adhesion strength develops from 2 days to 3 days, following mixing and application to a surface. In general, full adhesion strength as well as other properties of cured compositions of the present disclosure becomes fully developed within 7 days following mixing and application of a curable composition to a surface.

[0194] Cured compositions disclosed herein, such as cured sealants, exhibit properties acceptable for use in aerospace applications. In general, it is desirable that sealants used in aviation and aerospace applications exhibit the following properties: peel strength greater than 20 pounds per linear inch (pli) on Aerospace Material Specification (AMS) 3265B substrates determined under dry conditions, following immersion in JRF Type I for 7 days, and following immersion in a solution of 3% NaCl according to AMS 3265B test specifications; tensile strength between 300 pounds per square inch (psi) and 400 psi; tear strength greater than 50 pounds per linear inch (pli); elongation between 250% and 300%; and hardness greater than 40 Durometer A. These and other cured sealant properties appropriate for aviation and aerospace applications are disclosed in AMS 3265B. It is also desirable that, when cured, compositions of the present disclosure used in aviation and aircraft applications exhibit a percent volume swell not greater than 25% following immersion for one week at 60 °C (140 °F) and ambient pressure in JRF Type I. Other properties, ranges, and/or thresholds may be appropriate for other sealant applications.

[0195] In certain embodiments, therefore, compositions provided by the present disclosure are fuel-resistant. As used herein, the term "fuel resistant" means that a composition, when applied to a substrate and cured, can provide a cured product, such as a sealant, that exhibits a percent volume swell of not greater than 40%, in some cases not greater than 25%, in some cases not greater than 20%, in yet other cases not more than 10%, after immersion for one week at 140 °F (60 °C) and ambient pressure in Jet Reference Fluid (JRF) Type I according to methods similar to those described in ASTM D792 (American Society for Testing and Materials) or AMS 3269 (Aerospace Material Specification). Jet Reference Fluid (JRF) Type I, as employed for determination of fuel resistance, has the following composition: toluene: 28% ± 1% by volume; cyclohexane (technical): 34% ± 1% by volume; isooctane: 38% ± 1% by volume; and tertiary dibutyl disulfide: 1% ± 0.005% by volume (see AMS 2629, issued July 1, 1989, § 3.1.1 etc., available from SAE (Society of Automotive Engineers)).

[0196] In certain embodiments, compositions provided herein provide a cured product, such as a sealant, exhibiting a tensile elongation of at least 100% and a tensile strength of at least 400 psi when measured in accordance with the procedure described in AMS 3279, § 3.3.17.1, test procedure AS5127/1, § 7.7.

[0197] In certain embodiments, compositions provide a cured product, such as a sealant, that exhibits a lap shear strength of greater than 200 psi, such as at least 220 psi, at least 250 psi, and, in some cases, at least 400 psi, when measured according to the procedure described in SAE AS5127/1 paragraph 7.8.

[0198] In certain embodiments, a cured sealant comprising a composition provided by the present disclosure meets or exceeds the requirements for aerospace sealants as set forth in AMS 3277.

[0199] Apertures, including apertures of aerospace vehicles, sealed with compositions provided by the present disclosure are also disclosed.

[0200] In certain embodiments, a cured sealant provided by the present disclosure exhibits the following properties when cured for 2 days at room temperature, 1 day at 140 °F, and 1 day at 200 °F: a dry hardness of 49, a tensile strength of 428 psi, and an elongation of 266%; and after 7 days in JRF Type I, a hardness of 36, a tensile strength of 312 psi, and an elongation of 247%.

[0201] In certain embodiments, compositions provided by the present disclosure exhibit a Shore A hardness (following 7-day cure) greater than 10, greater than 20, greater than 30, and in certain embodiments, greater than 40; a tensile strength greater than 10 psi, greater than 100 psi, greater than 200 psi, and in certain embodiments, greater than 500 psi; an elongation greater than 100%, greater than 200%, greater than 500%, and in certain embodiments, greater than 1,000%; and a swell following exposure to JRF Type I (7 days) less than 20%.

EXAMPLES

[0202] Embodiments provided by the present disclosure are further illustrated by reference to the following examples, which describe the synthesis, properties, and uses of certain sulfur-containing polymers, maleimide adducts, and compositions comprising sulfur-containing polymers, maleimide adducts, and maleimides. It will be apparent to those skilled in the art that many modifications, both to materials, and methods, may be practiced without departing from the scope of the disclosure.

Example 1

Synthesis of Thiol-Terminated Polythioether Prepolymer

[0203] In a 189.3 l (50-gallon) reactor, 58.06 kg (128 lbs) of diethylene glycol divinyl ether (DEG-DVE) and 78.47 kg (173 lbs) of dimercaptodioxaoctane (DMDO) were mixed with 6 lbs of triallylcyanurate (TAC) and heated to 77 °C. To the heated reaction mixture was added 90.7 g (0.2 lb) of an azobisnitrile free radical catalyst (Vazo™ 67, 2,2'-azobis(2-methylbutyronitrile), DuPont). The reaction proceeded substantially to completion after 24 hours to afford a liquid thiol-terminated resin having a mercaptan equivalent weight of 1,522.

Example 2

Synthesis of Maleimide-Terminated Polythioether Prepolymer

[0204] 1,1'-(Methylenedi-4,1-phenylene)-bismaleimide (MDPBM, 8.96 g, 0.05 equivalents) was charged into a 500-mL, 3-necked round-bottomed flask followed by tetrahydrofuran (THF, 81 g). The flask was equipped with a mechanical stirrer, a reflux condenser that was connected to nitrogen-inlet and a temperature probe. Heating the mixture while stirring at the boiling point of THF produced a clear solution. Ethanol (41.34 g) was slowly introduced into the warm solution. A solution of a mercaptan-capped polythioether of functionality 2.21 (39.68 g, 0.0025 equivalents) in THF (~42 g) was dropped over a period of 1 h, 15 min at a temperature of 42 °C to 23 °C. The contents were heated at 68 °C for 22 h. A high value of mercaptan equivalent (532,200) indicated completion of the reaction. The solvent was removed under atmospheric distillation and vacuum (7-8 mmHg). A mixture (1:1, v/v) of toluene and methyl ethyl ketone (16.2 g) was introduced under stirring to dissolve the residue and produce a solution of 75% concentration; olefin equivalent weight: 2594 (calculated value); viscosity: 12.1 Pas (121P) (Brookfield Cap 2000; spindle no.: 6; rpm: 100). The product was a maleimide-terminated polythioether.

Example 3

Sealant Composition

[0205] The maleimide-terminated prepolymer of Example 2 (18.68 g, 0.0072 equivalents) was charged into a mixing cup (size: 60 g; Hauschild Mixer; model: DAC 600FVZ). Calcium carbonate (Socal® N2R; 16.53 g) was charged in three portions; each charge was followed by mixing in Hauschild mixer for 30 seconds. The contents were mixed in a Hauschild mixer (twice for 4 min), hand-mixed, and mixed again in the Hauschild mixer for 4 min. The mixture was left open for 1.5 h to evaporate solvents. A mercaptan-capped polythioether of functionality 2.21 (10.28 g, 0.0065 equivalents) and another mercaptan-capped polythioether of functionality 2.8 (1.14 g, 0.0007 equivalents; both polymers are available

from PPG Aerospace) were added. The contents were hand-mixed, mixed in the Hauschild mixer for 30 seconds, and a test specimen was made with approximate dimensions of 3 inches by 5 inches. The test specimen was subjected to a cure cycle of 20 h at room temperature, 9 h at 60 °C and 16 h at 93 °C. The cured sealant had the following properties; hardness: 57 (Shore A); tensile strength: 4.8 MPa (693 psi); elongation: 413%.

Example 4

Sealant Composition

[0206] The maleimide-terminated prepolymer of Example 2 (11.63 g) was charged into a mixing cup (size: 60 g; Hauschild Mixer; model: DAC 600FVZ). Calcium carbonate (Socal® N2R; 19.27 g) was charged in three portions; each charge was followed by mixing in Hauschild mixer for 30 seconds. The contents were mixed in a Hauschild mixer for (twice for 4 min), hand-mixed, and mixed again in the Hauschild mixer for 4 min. The mixture was left open for 1.5 h to evaporate solvents. A mercaptan-capped polythioether (20.18 g, Permapol® 3.1E available from PPG Aerospace) was added. The contents were hand-mixed, mixed in the Hauschild mixer for 30 seconds, and a test specimen was made with approximate dimensions of 3 inches by 5 inches. The test specimen was subjected to a cure cycle of 2 days at room temperature, and 1 day at 60 °C. The cured sealant had the following properties; hardness: 62 (Shore A); tensile strength: 4.7 MPa (682 psi); elongation: 420%.

Comparative Example 1

Sealant Composition with Thiol-terminated polythioether

[0207] A comparative sealant composition was prepared using the procedure described in Example 14 of U.S. Patent No. 6,172,179.

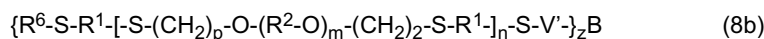
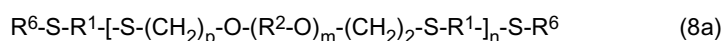
[0208] In a 2 L flask, 524.8 g (3.32 mol) of diethylene glycol divinyl ether (DEG-DVE) and 706.7 g (3.87 mol) of dimercaptodioxaoctane (DMDO) were mixed with 19.7 g (0.08 mol) of triallylcyanurate (TAC) and heated to 77°C. To the heated reaction mixture was added 4.6 g (0.024 mol) of an azobisnitrile free radical catalyst (VAZO®67 [2,2'-azobis(2-methylbutyronitrile), commercially available from DuPont.). The reaction proceeded substantially to completion after 2 hours to afford 1250 g (0.39 mol, yield 100%) of a liquid polythioether resin having a T_g of -68°C and a viscosity of 6.5 Pas (65 poise). The resin was faintly yellow and had low odor.

[0209] A sealant composition including the DMDO/DEG-DVE polythioether polymer was compounded as follows (amounts in parts by weight (pbw)): 100 pbw of the polythioether prepared in the previous paragraph; 60 pbw calcium carbonate; 1 pbw magnesium oxide; 1 pbw phenolic resin; 1 pbw DMP-30; and 3 pbw isopropyl alcohol.

[0210] The compounded polythioether polymer composition was mixed with an epoxy resin curing agent consisting of 22 wt% epoxy novalac, 34 wt% hydantoin epoxy, 34 wt% calcium carbonate, 5 wt% carbon black, and 5 wt% silane adhesion promoter, in a weight ratio of 10:1 and cured at ambient temperature and humidity. The following physical properties were obtained for the cured composition: cure hardness at 25°C of 60 Shore A; tensile strength at break 3.8 MPa (550 psi) ; elongation at break 600%; notched tear strength 100 p/l; low-temperature flexibility passed AMS 3267 § 4.5.4.7 low-temperature flexibility test.

Claims

1. A sulfur-containing maleimide adduct comprising at least two terminal maleimide groups.
2. The adduct of claim 1, wherein the sulfur-containing maleimide adduct comprises a polythioether, a polysulfide, sulfur-containing polyformal, or a combination of any of the foregoing.
3. The adduct of claim 1, wherein the adduct comprises a polythioether maleimide adduct of Formula (8a), a polythioether maleimide adduct of Formula (8b), or a combination thereof:



wherein:

each R^1 independently comprises C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, and/or $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein:

s is an integer from 2 to 6;
q is an integer from 1 to 5;
r is an integer from 2 to 10;

each R^3 is independently selected from hydrogen and methyl; and
each X is independently selected from -O-, -S-, and -NR-, wherein R is selected from hydrogen and methyl;
each R^2 independently comprises C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, and $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein s, q, r, R^3 , and X are as defined for R^1 ;

m is an integer from 0 to 50;
n is an integer from 1 to 60;
p is an integer from 2 to 6;

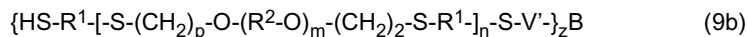
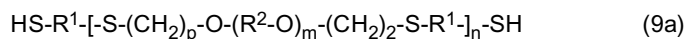
B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent $B(-V)_z$ wherein:

z is an integer from 3 to 6; and
each V is a group comprising a group reactive with thiol groups; and
each -V- is derived from the reaction of -V with a thiol; and
each R^6 is independently a moiety comprising a terminal maleimide group.

4. The adduct of claim 1, wherein the adduct comprises the reaction products of reactants comprising:

(a) a sulfur-containing polymer; and
(b) a compound having a terminal maleimide group and a group that is reactive with a terminal group of the sulfur-containing polymer.

5. The adduct of claim 4, wherein the sulfur-containing polymer comprises a thiol-terminated polythioether comprising a thiol-terminated polythioether polymer of Formula (9a), a thiol-terminated polythioether polymer of Formula (9b), or a combination thereof:



wherein:

each R^1 independently comprises C_{2-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, C_{5-8} heterocycloalkanediyl, or $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein:

s is an integer from 2 to 6;
q is an integer from 1 to 5;
r is an integer from 2 to 10;

each R^3 is independently selected from hydrogen and methyl; and
each X is independently selected from -O-, -S-, and -NR-, wherein R is selected from hydrogen and methyl;
each R^2 independently comprises C_{1-10} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-14} alkanecycloalkanediyl, or $-[(CHR^3)_s-X]_q-(CHR^3)_r-$, wherein s, q, r, R^3 , and X are as defined for R^1 ;

m is an integer from 0 to 50;
n is an integer from 1 to 60;
p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent $B(-V)_z$ wherein:

z is an integer from 3 to 6; and
each -V is a group comprising a terminal group reactive with thiol groups; and

each -V'- is derived from the reaction of -V with a thiol.

6. The adduct of claim 4, wherein the compound having a terminal maleimide group and a group that is reactive with a terminal group of the sulfur-containing polymer comprises 1,1'-(methylenedi-4,1-phenylene)bismaleimide.

7. A composition comprising:

- (a) a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups; and
(b) a compound having at least two maleimide groups.

8. The composition of claim 7, wherein

- the compound having at least two maleimide groups comprises 1,1'-(methylenedi-4,1-phenylene)bismaleimide;
or
- the compound having at least two maleimide groups comprises the adduct of claim 1; or
- the sulfur-containing polymer comprises a polythioether.

9. A composition comprising:

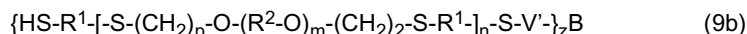
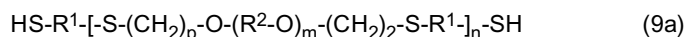
- (a) the sulfur-containing maleimide adduct of claim 1; and
(b) a curing agent comprising at least two terminal groups that are reactive with maleimide groups.

10. The composition of claim 9, wherein the curing agent comprises

- (a) a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups, a monomeric thiol, a polythiol, or a combination of any of the foregoing; or
(b) comprises a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups.

11. The composition of claim 10(b), wherein the sulfur-containing polymer comprises a polythioether.

12. The composition of claim 11, wherein the sulfur-containing polythioether comprises a thiol-terminated polythioether comprising a thiol-terminated polythioether polymer of Formula (9a), a thiol-terminated polythioether polymer of Formula (9b), or a combination thereof:



wherein:

each R¹ independently comprises C₂₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₄ alkanecycloalkanediyl, C₅₋₈ heterocycloalkanediyl, or -[(-CHR³)_s-X]_q-(-CHR³)_r-, wherein:

s is an integer from 2 to 6;
q is an integer from 1 to 5;
r is an integer from 2 to 10;

each R³ is independently selected from hydrogen and methyl; and

each X is independently selected from -O-, -S-, and -NR-, wherein R is selected from hydrogen and methyl;

each R² independently comprises C₁₋₁₀ alkanediyl, C₆₋₈ cycloalkanediyl, C₆₋₁₄ alkanecycloalkanediyl, or -[(-CHR³)_s-X]_q-(-CHR³)_r-, wherein s, q, r, R³, and X are as defined as for R¹;

m is an integer from 0 to 50;
n is an integer from 1 to 60;
p is an integer from 2 to 6;

B represents a core of a z-valent, vinyl-terminated polyfunctionalizing agent B(-V)_z wherein:

z is an integer from 3 to 6; and

each V is a group comprising a terminal group reactive with thiol groups; and
each -V'- is derived from the reaction of -V with a thiol.

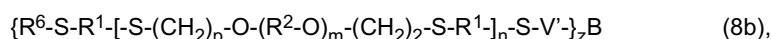
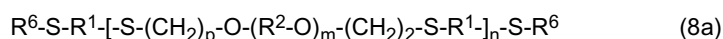
13. The composition of claim 9 comprising:

- (a) the sulfur-containing maleimide adduct of claim 1;
- (b) a sulfur-containing polymer comprising at least two terminal groups reactive with maleimide groups; and
- (c) a monomeric compound having at least two maleimide groups.

14. A sealant comprising the sulfur-containing maleimide adduct of claim 1, wherein the sealant is optionally cured.

Patentansprüche

1. Schwefelhaltiges Maleinimidaddukt enthaltend wenigstens zwei endständige Maleinimidgruppen.
2. Addukt nach Anspruch 1, wobei das schwefelhaltige Maleinimidaddukt einen Polythioether, ein Polysulfid, schwefelhaltiges Polyformal oder eine Kombination jeder der angegebenen enthält.
3. Addukt nach Anspruch 1, wobei das Addukt ein Polythioethermaleinimidaddukt der Formel (8a), ein Polythioethermaleinimidaddukt der Formel (8b), oder eine Kombination davon enthält:



worin:

jedes R^1 unabhängig voneinander C_{2-10} -Alkandiyl, C_{6-8} -Cycloalkandiyl, C_{6-10} -Alkancycloalkandiyl, C_{5-8} -eterocycloalkandiyl und/oder $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$ umfasst, worin:

s eine ganze Zahl von 2 bis 6 ist,
q eine ganze Zahl von 1 bis 5 ist,
r eine ganze Zahl von 2 bis 10 ist,

jedes R^3 unabhängig voneinander ausgewählt ist aus Wasserstoff und Methyl und
jedes X unabhängig voneinander ausgewählt ist aus -O-, -S- und -NR-, worin R ausgewählt ist aus Wasserstoff und Methyl,

jedes R^2 unabhängig voneinander C_{1-10} -Alkandiyl, C_{6-8} -Cycloalkandiyl, C_{6-14} -Alkancycloalkandiyl und $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$ umfasst, worin s, q, r, R^3 und X wie für R^1 definiert sind;

m eine ganze Zahl von 0 bis 50 ist,
n eine ganze Zahl von 1 bis 60 ist,
p eine ganze Zahl von 2 bis 6 ist,

B für einen Kern eines z-valenten Polyfunktionalisierungsmittels $B(-V)_z$ mit endständigen Vinylgruppen steht, worin:

z eine ganze Zahl von 3 bis 6 ist und
jedes V eine Gruppe ist, die eine Gruppe enthält, die mit Thiolgruppen reaktiv ist, und
jedes -V'- sich von der Reaktion von -V mit einem Thiol ableitet und
jedes R^6 unabhängig voneinander eine Einheit ist, die eine endständige Maleinimidgruppe enthält.

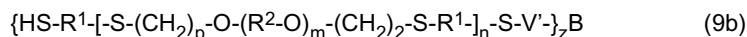
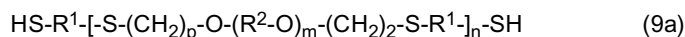
4. Addukt nach Anspruch 1, wobei das Addukt die Reaktionsprodukte von Reaktanten enthält, die:

- (a) ein schwefelhaltiges Polymer und
- (b) eine Verbindung mit einer endständigen Maleinimidgruppe und einer Gruppe, die mit einer endständigen

Gruppe des schwefelhaltigen Polymers reaktiv ist,

umfassen.

5. Addukt nach Anspruch 4, wobei das schwefelhaltige Polymer einen Polythioether mit endständigen Thiolgruppen enthält, der ein Polythioetherpolymer der Formel (9a) mit endständigen Thiolgruppen, ein Polythioetherpolymer der Formel (9b) mit endständigen Thiolgruppen oder eine Kombination davon enthält:



jedes R^1 unabhängig voneinander C_{2-10} -Alkandiyl, C_{6-8} -Cydoalkandiyl, C_{6-14} -Alkancycloalkandiyl, C_{5-8} -Heterocycloalkandiyl oder $\text{[-(CHR}^3\text{)}_s\text{-X]}_q\text{-(CHR}^3\text{)}_r$ umfasst, worin:

s eine ganze Zahl von 2 bis 6 ist,
q eine ganze Zahl von 1 bis 5 ist,
r eine ganze Zahl von 2 bis 10 ist,

jedes R^3 unabhängig voneinander ausgewählt ist aus Wasserstoff und Methyl und
jedes X unabhängig voneinander ausgewählt ist aus -O-, -S- und -NR-, worin R ausgewählt ist aus Wasserstoff und Methyl,

jedes R^2 unabhängig voneinander C_{1-10} -Alkandiyl, C_{6-8} -Cycloalkandiyl, C_{6-14} -Alkancycloalkandiyl oder $\text{[-(CHR}^3\text{)}_s\text{-X]}_q\text{-(CHR}^3\text{)}_r$ umfasst, worin s, q, r, R^3 und X wie für R^1 definiert sind,

m eine ganze Zahl von 0 bis 50 ist,
n eine ganze Zahl von 1 bis 60 ist,
p eine ganze Zahl von 2 bis 6 ist,

B für den Kern eines z-valenten Polyfunktionalisierungsmittels B(-V)_z mit endständigen Vinylgruppen steht, worin:

z eine ganze Zahl von 3 bis 6 ist und
jedes -V eine Gruppe ist, die eine endständige Gruppe enthält, die mit Thiolgruppen reaktiv ist, und
jedes -V' sich von der Reaktion von -V mit einem Thiol ableitet.

6. Addukt nach Anspruch 4, wobei die Verbindung mit einer endständigen Maleinimidgruppe und einer Gruppe, die mit einer endständigen Gruppe des schwefelhaltigen Polymers reaktiv ist, 1,1'-(Methylendi-4,1-phenylen)bismaleimid enthält.

7. Zusammensetzung enthaltend:

(a) ein schwefelhaltiges Polymer mit wenigstens zwei endständigen Gruppen, die mit Maleinimidgruppen reaktiv sind, und
(b) eine Verbindung mit wenigstens zwei Maleinimidgruppen.

8. Zusammensetzung nach Anspruch 7, wobei:

- die Verbindung mit wenigstens zwei Maleinimidgruppen 1,1'-(Methylendi-4,1-phenylen)bismaleimid enthält oder
- die Verbindung mit wenigstens zwei Maleinimidgruppen das Addukt nach Anspruch 1 enthält oder
- das schwefelhaltige Polymer einen Polythioether enthält.

9. Zusammensetzung enthaltend:

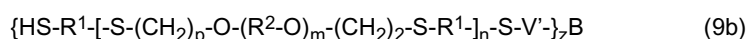
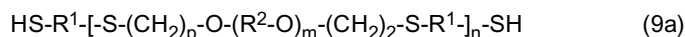
(a) das schwefelhaltige Maleinimidaddukt nach Anspruch 1 und
(b) ein Härtungsmittel, das wenigstens zwei endständige Gruppen enthält, die mit Maleinimidgruppen reaktiv sind.

10. Zusammensetzung nach Anspruch 9, wobei das Härtungsmittel

- (a) ein schwefelhaltiges Polymer mit wenigstens zwei endständigen Gruppen, die mit Maleinimidgruppen reaktiv sind, ein monomeres Thiol, ein Polythiol oder eine Kombination jeder der vorgenannten enthält oder
 (b) ein schwefelhaltiges Polymer mit wenigstens zwei endständigen Gruppen, die mit Maleinimidgruppen reaktiv sind, enthält.

11. Zusammensetzung nach Anspruch 10(b), wobei das schwefelhaltige Polymer einen Polythioether enthält.

12. Zusammensetzung nach Anspruch 11, wobei der schwefelhaltige Polythioether einen Polythioether mit endständigen Thiolgruppen enthält, der ein Polythioetherpolymer der Formel (9a) mit endständigen Thiolgruppen, ein Polythioetherpolymer der Formel (9b) mit endständigen Thiolgruppen oder eine Kombination davon enthält:



jedes R^1 unabhängig C_{2-10} -Alkandiyl, C_{6-8} -Cycloalkandiyl, C_{6-14} -Alkancycloalkandiyl, C_{5-8} -Heterocycloalkandiyl oder $\text{[-(CHR}^3\text{)-}_s\text{-X-]}_q\text{-(CHR}^3\text{)-}_r$ umfasst, worin:

- s eine ganze Zahl von 2 bis 6 ist,
 q eine ganze Zahl von 1 bis 5 ist,
 r eine ganze Zahl von 2 bis 10 ist,

jedes R^3 unabhängig voneinander ausgewählt ist aus Wasserstoff und Methyl und
 jedes X unabhängig voneinander ausgewählt ist aus -O-, -S- und -NR-, worin R aus Wasserstoff und Methyl ausgewählt ist,

jedes R^2 unabhängig voneinander C_{1-10} -Alkandiyl, C_{6-8} -Cycloalkandiyl, C_{6-14} -Alkancycloalkandiyl oder $\text{[-(CHR}^3\text{)-}_s\text{-X-]}_q\text{-(CHR}^3\text{)-}_r$ umfasst, worin s, q, r, R^3 und X wie für R^1 definiert sind,

- m eine ganze Zahl von 0 bis 50 ist,
 n eine ganze Zahl von 1 bis 60 ist,
 p eine ganze Zahl von 2 bis 6 ist,

B für den Kern eines z-valenten Polyfunktionalisierungsmittels B(-V)_z mit endständigen Vinylgruppen steht, worin:

- z eine ganze Zahl von 3 bis 6 ist und
 jedes V eine Gruppe ist, die eine endständige Gruppe enthält, die mit Thiolgruppen reaktiv ist, und
 jedes -V'- sich von der Reaktion von -V mit einem Thiol ableitet.

13. Zusammensetzung nach Anspruch 9 enthaltend:

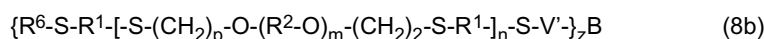
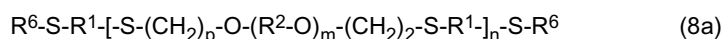
- (a) das schwefelhaltige Maleinimidaddukt nach Anspruch 1,
 (b) ein schwefelhaltiges Polymer, das wenigstens zwei endständige Gruppen enthält, die mit Maleinimidgruppen reaktiv sind, und
 (c) eine monomere Verbindung mit wenigstens zwei Maleinimidgruppen.

14. Ein Dichtmittel enthaltend das schwefelhaltige Maleinaddukt nach Anspruch 1, wobei das Dichtmittel optional gehärtet ist.

Revendications

1. Adduit de maléimide sulfuré, comprenant au moins deux groupes maléimido terminaux.
 2. Adduit conforme à la revendication 1, lequel adduit de maléimide sulfuré comprend un polythioéther, un polysulfure, un polyformal sulfuré, ou une combinaison de n'importe quels composés de ces types.

3. Adduit conforme à la revendication 1, lequel adduit comprend un adduit de maléimide sur polythioéther de formule (8a), un adduit de maléimide sur polythioéther de formule (8b), ou une combinaison de tels adduits :



dans lesquelles formules

- chaque symbole R^1 représente indépendamment un groupe alcane-diyle en C_{2-10} , cycloalcane-diyle en C_{6-8} , alcane-cycloalcane-diyle en C_{6-10} ou hétérocycloalcane-diyle en C_{5-8} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, dans laquelle

- l'indice s est un nombre entier valant de 2 à 6,
- l'indice q est un nombre entier valant de 1 à 5,
- l'indice r est un nombre entier valant de 2 à 10,
- chaque symbole R^3 représente indépendamment un atome d'hydrogène ou un groupe méthyle,
- et chaque symbole X représente indépendamment un chaînon symbolisé par $-O-$, $-S-$ ou $-NR-$ où R représente un atome d'hydrogène ou un groupe méthyle ;

- chaque symbole R^2 représente indépendamment un groupe alcane-diyle en C_{1-10} , cycloalcane-diyle en C_{6-8} ou alcane-cycloalcane-diyle en C_{6-14} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, dans laquelle les indices s , q et r et les symboles R^3 et X ont les valeurs et significations indiquées à propos de R^1 ;

- l'indice m est un nombre entier valant de 0 à 50 ;
- l'indice n est un nombre entier valant de 1 à 60 ;
- l'indice p est un nombre entier valant de 2 à 6 ;
- B représente le coeur d'un agent de polyfonctionnalisation, à groupes terminaux vinyle et de valence z , de formule $B(-V)_z$ dans laquelle

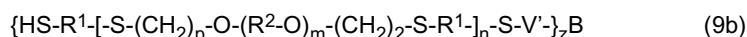
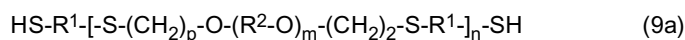
- l'indice z est un nombre entier valant de 3 à 6,
- et chaque symbole V représente un fragment comprenant un groupe réactif vis-à-vis du groupe sulfhydryle ;

- chaque symbole V' représente un fragment issu de la réaction d'un fragment V avec un thiol ;
- et chaque symbole R^6 représente indépendamment un fragment comprenant un groupe maléimido terminal.

4. Adduit conforme à la revendication 1, lequel adduit comprend les produits de réaction de réactifs comprenant :

- a) un polymère sulfuré,
- b) et un composé qui comporte un groupe terminal maléimido et un groupe réactif vis-à-vis d'un groupe terminal du polymère sulfuré.

5. Adduit conforme à la revendication 4, dans lequel le polymère sulfuré comprend un polythioéther à terminaisons thiol, comprenant un polymère de type polythioéther à terminaisons thiol de formule (9a), un polymère de type polythioéther à terminaisons thiol de formule (9b), ou une combinaison de tels polymères :



dans lesquelles formules

- chaque symbole R^1 représente indépendamment un groupe alcane-diyle en C_{2-10} , cycloalcane-diyle en C_{6-8} , alcane-cycloalcane-diyle en C_{6-14} ou hétérocycloalcane-diyle en C_{5-8} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, dans laquelle

- l'indice s est un nombre entier valant de 2 à 6,
- l'indice q est un nombre entier valant de 1 à 5,
- l'indice r est un nombre entier valant de 2 à 10,

- chaque symbole R^3 représente indépendamment un atome d'hydrogène ou un groupe méthyle,
- et chaque symbole X représente indépendamment un chaînon symbolisé par -O- -S- ou -NR- où R représente un atome d'hydrogène ou un groupe méthyle ;

- chaque symbole R^2 représente indépendamment un groupe alcane-diyle en C_{1-10} , cycloalcane-diyle en C_{6-8} ou alcane-cycloalcane-diyle en C_{6-14} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CMR^3)_r-$, dans laquelle les indices s, q et r et les symboles R^3 et X ont les valeurs et significations indiquées à propos de R^1 ;

- l'indice m est un nombre entier valant de 0 à 50 ;

- l'indice n est un nombre entier valant de 1 à 60 ;

- l'indice p est un nombre entier valant de 2 à 6 ;

- B représente le coeur d'un agent de polyfonctionnalisation, à groupes terminaux vinyle et de valence z, de formule $B(-V)_z$ dans laquelle

- l'indice z est un nombre entier valant de 3 à 6,

- et chaque symbole V représente un fragment comprenant un groupe réactif vis-à-vis du groupe sulfhydryle ;

- et chaque symbole V' représente un fragment issu de la réaction d'un fragment V avec un thiol.

6. Adduit conforme à la revendication 4, dans lequel le composé qui comporte un groupe terminal maléimido et un groupe réactif vis-à-vis d'un groupe terminal du polymère sulfuré comprend du 1,1'-(méthylène-di-4,1-phénylène)-bis-maléimide.

7. Composition comprenant :

- a) un polymère sulfuré comportant au moins deux groupes terminaux réactifs vis-à-vis d'un groupe maléimido,
- b) et un composé qui comporte au moins deux groupes maléimido.

8. Composition conforme à la revendication 7, dans laquelle

- le composé comportant au moins deux groupes maléimido comprend du 1,1'-(méthylène-di-4,1-phénylène)-bis-maléimide,

- ou le composé comportant au moins deux groupes maléimido comprend un adduit conforme à la revendication 1,

- ou le polymère sulfuré comprend un polythioéther.

9. Composition comprenant :

a) un adduit de maléimide sulfuré, conforme à la revendication 1,

b) et un agent durcisseur comportant au moins deux groupes terminaux réactifs vis-à-vis d'un groupe maléimido.

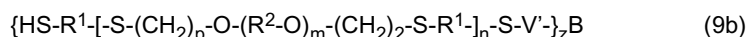
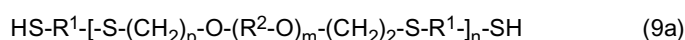
10. Composition conforme à la revendication 9, dans laquelle l'agent durcisseur:

a) comprend un polymère sulfuré comportant au moins deux groupes terminaux réactifs vis-à-vis d'un groupe maléimido, un monothiol, un polythiol ou une combinaison de tels composés,

b) ou comprend un polymère sulfuré comportant au moins deux groupes terminaux réactifs vis-à-vis d'un groupe maléimido.

11. Composition conforme à la revendication 10, item (b), dans laquelle le polymère sulfuré comprend un polythioéther.

12. Composition conforme à la revendication 11, dans laquelle le polythioéther sulfuré comprend un polythioéther à terminaisons thiol comprenant un polymère de type polythioéther à terminaisons thiol de formule (9a), un polymère de type polythioéther à terminaisons thiol de formule (9b), ou une combinaison de tels polymères :



dans lesquelles formules

- chaque symbole R^1 représente indépendamment un groupe alcane-diyle en C_{2-10} , cycloalcane-diyle en C_{6-8} , alcane-cycloalcane-diyle en C_{6-14} ou hétérocycloalcane-diyle en C_{5-8} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, dans laquelle

- l'indice s est un nombre entier valant de 2 à
- l'indice q est un nombre entier valant de 1 à 5,
- l'indice r est un nombre entier valant de 2 à 10,
- chaque symbole R^3 représente indépendamment un atome d'hydrogène ou un groupe méthyle,
- et chaque symbole X représente indépendamment un chaînon symbolisé par -O-, -S- ou -NR- où R représente un atome d'hydrogène ou un groupe méthyle ;

- chaque symbole R^2 représente indépendamment un groupe alcane-diyle en C_{1-10} , cycloalcane-diyle en C_{6-8} ou alcane-cycloalcane-diyle en C_{6-14} , ou un groupe de formule $-[(-CHR^3)_s-X]_q-(-CHR^3)_r-$, dans laquelle les indices s, q et r et les symboles R^3 et X ont les valeurs et significations indiquées à propos de R^1 ;

- l'indice m est un nombre entier valant de 0 à 50 ;
- l'indice n est un nombre entier valant de 1 à 60 ;
- l'indice p est un nombre entier valant de 2 à 6 ;
- B représente le coeur d'un agent de polyfonctionnalisation, à groupes terminaux vinyle et de valence z, de formule $B(-V)_z$ dans laquelle

- l'indice z est un nombre entier valant de 3 à
- et chaque symbole V représente un fragment comprenant un groupe réactif vis-à-vis du groupe sulfhydryle ;

- et chaque symbole V' représente un fragment issu de la réaction d'un fragment V avec un thiol.

13. Composition conforme à la revendication 9, comprenant :

- a) un adduit de maléimide sulfuré, conforme à la revendication 1,
- b) un polymère sulfuré comportant au moins deux groupes terminaux réactifs vis-à-vis d'un groupe maléimido,
- c) et un composé monomère comportant au moins deux groupes maléimido.

14. Agent d'étanchéité comprenant un adduit de maléimide sulfuré conforme à la revendication 1, lequel agent d'étanchéité, en option, est durci.

REFERENCES CITED IN THE DESCRIPTION

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