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(54) Title of the Invention: **Compositions comprising an acrylic polymer and processes of preparing the same**
Abstract Title: **Composites comprising a crosslinked acrylic polymer**

(57) A composite comprised of a mineral and a cross-linked polymer, characterized by a cross-linking density in the range of from $2x10^{20}$ to $2x10^{25}$ units/l, is disclosed. Process of preparing the composite is also disclosed. The polymer comprises at least one crosslinker and a polymeric backbone comprising a plurality of momoneric units. The mineral may be a ceramic such as alumina, quartz, zirconia, calcium carbonate, clay etc. The composite could be used for engineering stones, artificial marble etc. A similar composition can be made by mixing monomers, crosslinker, initiator and optionally a toughener, adding a mineral to the mixture, and curing at above 90 degrees C.

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COMPOSITIONS COMPRISING AN ACRYLIC POLYMER AND PROCESSES OF PREPARING THE SAME

FIELD OF INVENTION

[001] This invention, in some embodiments thereof, is directed to a composite comprising a crosslinked acrylic polymer, and a mineral.

BACKGROUND OF THE INVENTION

[002] Engineered stones are widely used as building materials e.g., for kitchen counter tops, indoor and outdoor floors, dressing tables, bathtubs, wash bowls, and interior articles. These artificial marbles are generally manufactured from unsaturated polyester thermoset compositions that comprise e.g., vinyl monomeric units, styrene as a reactive solvent and cobalt-octoate as a curing process accelerator. One disadvantage of these known engineered stone compositions is the tendency of the styrene moiety to shrink which might cause micro- and macro- cracks and decrease the bending strength and toughness.

SUMMARY OF THE INVENTION

[003] The present invention, in some embodiments thereof, is directed to a composite comprising a crosslinked acrylic polymer, and a mineral.

[004] According to some embodiments of the present invention, there is provided a composition comprising a composite, the composite comprising a cross-linked polymer and at least one mineral, wherein:

(i) the cross-linked polymer comprises at least one cross-linker and a polymeric backbone comprising a plurality of monomeric units; and

(ii) the cross-linked polymer is characterized by a cross-linking density in the range of from $2x10^{20}$ to $2x10^{25}$ units/l, by total weight of the polymer.

[006] In some embodiments, the mineral comprises a ceramic material.

[007] In some embodiments, the ceramic material is selected from the group consisting of: alumina, quartz, zirconia, silicon carbide, silicon nitride, boron carbide, boron nitride, aluminum nitride, yttria, or any mixture thereof.

[008] In some embodiments, the mineral is selected from the group consisting of: quartz, clay, calcium carbonate, aluminum hydroxide, magnesium hydroxide, aluminum oxide or any combination thereof.

[009] In some embodiments, the concentration of the mineral is in the range of from 75% to 93%, by total weight of the composite.

[010] In some embodiments, the mineral is in the form of one or more particles.

[011] In some embodiments, a median diameter of the one or more particles is in the range of from 0.001 to 8 mm.

[012] In some embodiments, at least one monomeric unit comprises an acrylic monomeric unit.

[013] In some embodiments, at least one monomeric unit from the plurality of monomeric units is selected from the group consisting of: methyl methacrylate, 2-ethylhexyl acrylate, 2–ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, isobornyl acrylate, isobornyl methacrylate, acrylic acid, methacrylic acid and any derivative or combination thereof.

[014] In some embodiments, at least 45%, by weight, of the monomeric units are derived from one or more materials selected from the group consisting of: methacrylate, ethyl acrylate, or a combination thereof.

[015] In some embodiments, the cross-linker is selected from the group consisting of: trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol tetraacrylate, dipentaerithritol hexaacrylate, dendritic acrylates, and methacrylates having at least two functional groups, and any derivative or combination thereof.

[016] In some embodiments, the cross-linked polymer comprises from 5% to 30% acrylic polymer, by weight of the composite.

[017] In some embodiments, a concentration of the cross-linked polymer is in the range of from about 7% to 30%, by weight, of the composite.

[018] In some embodiments, the composite further comprises a toughener. In some embodiments, the toughener is selected from the group consisting of: polyurethanes mono acrylate, polyurethanes diacrylate, polyurethanes triacrylate, or any combination thereof. In some embodiments, the toughener is in the form of a core-shell structure.

[019] In some embodiments, the toughener is in amount ranging from 2% to 20%, by weight, of the cross-linked polymer.

[020] In some embodiments, the composite comprises less than 0.2%, by weight, of styrene monomeric units.

[021] In some embodiments, the composite comprises less than 0.01% of transition metals (e.g., cobalt).

[022] In some embodiments, the composite is characterized by a glass-transition temperature (T_g) in the range of from 65°C to 110°C.

[023] In some embodiments, the composite is characterized by young modulus in the range of from 13,000 to 30,000 MPa. In some embodiments, the composite is characterized by flexural strength in the range of from 45 to 110 MPa. In some embodiments, the composite is characterized by young modulus in the range of from 10,000 to 30,000 MPa.

[024] In some embodiments, the composite is characterized by toughness (G_{1c}) of at least 30 J/m^2.

[025] In some embodiments, the composite is characterized by heat distortion temperature (HDT) of at least 65°C. In some embodiments, the composite is characterized by whiteness index change (ΔWI) of less than 25% after 50-200 hours of UV radiation exposure.

[026] In some embodiments, the composite further comprises a linker attached to the polymeric backbone, wherein the linker is configured to contact the mineral.

[027] In some embodiments, the linker is physically attached to the mineral.

[028] In some embodiments, the linker is covalently attached to the polymeric backbone.

[029] In some embodiments, the linker is derived from acryloyl. In some embodiments, the linker comprises alkoxysilane. In some embodiments, the linker is in amount ranging from 0.02% to 0.3%, by weight, of the composite.

[030] According to another aspect, there is provided a method for obtaining a composition comprising a composite, the composite comprising a cross-linked polymer and at least one mineral, the method comprising the steps of:

a. mixing a plurality of monomers, at least one cross-linker, a peroxide initiator, and optionally at least one toughener or one or more polymer stabilizers, thereby obtaining a mixture of the cross-linked polymer;

b. adding a mineral to the mixture;

c. curing the mixture at a temperature above 90°C.

[031] In some embodiments, the curing step further comprises a step of adding a linker to the mixture.

[032] In some embodiments, the peroxide initiator is selected from the group consisting of: di-benzoyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, cyclohexanone peroxide, methylethyl peroxide, tert-butyl peroxyoctoate, tert-butyl peroxybenzoate, dicumyl peroxide, 1,1-bis(tert-butyl peroxy)3,3,5-trimethylcyclohexane, tert-butyl peroxymaleate, and any derivative or combination thereof.

[032] Unless otherwise defined, all technical and/or scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the invention, exemplary methods and/or materials are described below. In case of conflict, the patent specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and are not intended to be necessarily limiting.

DETAILED DESCRIPTION OF THE INVENTION

[033] The present invention, in some embodiments thereof, is directed to a composite comprising a cross linked polymeric backbone having acrylic monomeric units, and a mineral.

[034] Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not necessarily limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways.

The composition

[035] The present invention, in some embodiments thereof, relates to a composition comprising a composite, wherein the composite comprises a cross-linked polymer and at least one mineral, wherein the polymeric backbone comprises at least one acrylic group (also referred to as: "acrylic monomeric unit"). In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 15 moles% of the polymer.

[036] In some embodiments, the composite is in the form of a slab.

[037] In some embodiments, the composite is ultraviolet (U.V.) stable.

[038] In some embodiments, by "U.V. stable" it is meant that upon attacking the disclosed composite by ultraviolet radiation, the composite remains substantially integrated (not cracked). Further embodiments of the U.V. stability are described hereinbelow.

[039] The term "cross-linking density" refers to the density of the cross-links formed in the resulting "cross-linked polymer". The cross-linking percent may be calculated by using the percent solubility of the polymer of the acrylic polymer in solvent (e.g., toluene) indicating the relative cross-linking of the polymer.

[040] In some embodiments, the cross-linked polymer is characterized by a cross-linking density of less than 20 moles%, less than 16 moles%, less than 15 moles%, less than 14 moles%, less than 13 moles%, less than 12 moles%, less than 11 moles%, less than 10 moles%, less than 9 moles%, less than 8 moles%, less than 7 moles%, less than 6 moles%, or less than 5 moles% of the polymer.

[041] In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 20 moles% of the polymer. In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 15 moles% of the polymer. In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 12 moles% of the polymer. In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 10 moles% of the polymer. In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from 1 mole% to 7 moles% of the polymer.

[042] In some embodiments, the cross-linked polymer is devoid of tri-functional monomeric units.

[043] The term "%mole(s)" used herein refers to molar fraction or molar percentage of the cross-linked polymer.

[044] In some embodiments, the cross-linked polymer is characterized by a cross-linking density in the range of from $2x10^{20}$ to $3x10^{23}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-

linking density in the range of from $2x10^{20}$ to $2x10^{24}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{21}$ to $2x10^{24}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{22}$ to $2x10^{24}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{22}$ to $3x10^{23}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{20}$ to $2x10^{25}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{21}$ to $2x10^{25}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $2x10^{22}$ to $2x10^{25}$ units/l, by total weight of the polymer. In some embodiments, the cross-linked polymer is characterized by cross-linking density in the range of from $1x10^{23}$ to $3x10^{23}$ units/l, by total weight of the polymer.

[045] In some embodiments, the mineral comprises a ceramic material.

[046] In some embodiments, the ceramic material is selected from, without being limited thereto, alumina, quartz, zirconia, alumina, quartz, zirconia, titania, silica, magnesia, silicon carbide, silicon nitride, boron carbide, boron nitride, aluminum nitride, cordierite, sialon yttria, or any mixture thereof.

[047] In some embodiments, the mineral is selected from, without being limited thereto, quartz, clay, calcium carbonate, aluminum hydroxide, magnesium hydroxide, aluminum oxide, or any combination thereof. In some embodiments, the mineral is in the form of one or more particles. In exemplary embodiments, the mineral is quartz.

[048] In some embodiments, the particle is characterized by a diameter of less than 8 mm. In some embodiments, the particle is characterized by a diameter of less than 4 mm. In some embodiments, the particle is characterized by a diameter of from 0.0001 to 8 mm. In some embodiments, the particle is characterized by a diameter of from 0.001 to 8 mm. In some embodiments, the particle is characterized by a diameter of from 0.001 to 4 mm.

[049] In exemplary embodiments, the particles are classified into two, or, in some embodiments, three groups according to their size, referred to as: "large", "medium" and "small".

[050] Herein, the term "diameter" encompasses a size of at least one dimension, e.g., length. In some embodiments, the term "diameter" refers to a median size of a plurality of particles.

[051] In some embodiments, the small particles are characterized by a diameter of from 0.001 to 0.05 mm. In some embodiments, the small particles are characterized by a diameter of from 0.001 to 0.06 mm. In some embodiments, the small particles are characterized by a diameter of from 0.0001 to 0.06 mm. In some embodiments, the small particles are characterized by a diameter of from 0.5 to 0.8 mm. In some embodiments, the small particles are characterized by a diameter of from 0.4 to 1 mm.

[052] In some embodiments, the medium particles are characterized by a diameter of from 0.06 to 0.2 mm. In some embodiments, the medium particles are characterized by a diameter of from 0.05 to 0.3 mm. In some embodiments, the medium particles are characterized by a diameter of from 0.7 to 1.2 mm. In some embodiments, the medium particles are characterized by a diameter of from 0.5 to 1.5 mm. In some embodiments, the medium particles are characterized by a diameter of from 1.2 to 2.5 mm. In some embodiments, the medium particles are characterized by a diameter of from 1 to 2.6 mm. In some embodiments, the medium particles are characterized by a diameter of from 1 to 3 mm.

[053] In some embodiments, the large particles are characterized by a diameter of from 0.2 to 0.5 mm. In some embodiments, the large particles are characterized by a diameter of from 0.1 to 0.6 mm. In some embodiments, the large particles are characterized by a diameter of from 2.5 to 4 mm. In some embodiments, the large particles are characterized by a diameter of from 2 to 4 mm. In some embodiments, the large particles are characterized by a diameter of from 2 to 8 mm. In some embodiments, the large particles are characterized by a diameter of from 3 to 8 mm.

[054] In some embodiments, the weight ratio of the large, medium and small particles is in the range of from 3:0.8:2.5 to 10:3:8, or any value therebetween. In some embodiments, the weight ratio of the large, medium and small particles is in the range of from 6:1:4 to 5:1:4, respectively, or any value therebetween. In some embodiments,

the weight ratio of the large, medium and smallest particles is in the range of from 6:1:4 to 10:3:8, respectively, or any value therebetween. In some embodiments, the weight ratio of the large, medium and smallest particles is in the range of from 3:0.8:2.5 to 10:3:8, respectively, or any value therebetween. In some embodiments, the weight ratio of the large, medium and smallest particles is in the range of from 4:1:4 to 5:1:4, respectively, or any value therebetween. In some embodiments, the weight ratio of the large, medium and smallest particles is in the range of from 4:1:4 to 5:1:5, respectively, or any value therebetween. In some embodiments, the weight ratio of the large, medium and smallest particles is in the range of from 4:1:4 to 4:1:5, respectively, or any value therebetween.

[055] In some embodiments, the cross-linked polymer is characterized by a viscosity of at least 25, at least 50, at least 100, at least 150, at least 250, at least 400, at least 650, at least 800, at least 1,000, or at least 1,200 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity of less than 1,200, less than 1,000, less than 800, less than 650, less than 400, less than 250, less than 100, less than 50 or less than 25 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity in the range of from 50 to 1,000 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity in the range of from 250 to 650 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity in the range of from 25 to 1,200 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity in the range of from 50 to 1,200 cP. In some embodiments, the cross-linked polymer is characterized by a viscosity in the range of from 200 to 700 cP.

[056] In some embodiments, the polymeric backbone comprises acrylic monomeric units selected from, without being limited thereto, methyl methacrylate, 2-ethylhexyl acrylate, 2–ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, isobornyl acrylate, isobornyl methacrylate, or any monomeric unit derived from acrylic acid, methacrylic acid, or any derivative or combination thereof.

[057] In some embodiments, at least 30%, at least 40%, at least 45%, or at least 50%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate.

[058] In some embodiments, the cross-linked polymer comprises from 1% to 40%, or from 3% to 30%, or from 5% to 20%, acrylic polymer by weight of the composite.

[059] In some embodiments, less than 95%, less than 90%, less than 85%, less than 80%, less than 75%, less than 70%, less than 65%, less than 60%, less than 55% or less than 50%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate.

[060] In some embodiments, 40% to 95%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate. In some embodiments, 50% to 95%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate. In some embodiments, 40% to 90%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate. In some embodiments, 50% to 90%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate. In some embodiments, 80% to 95%, by weight, of the monomeric units in the polymeric backbone are derived from methacrylate.

[061] In some embodiments, the cross-linker is selected from, but is not limited to: tri-ethylene glycol di-methacrylate, polyethylene glycol di-acrylate, polyethylene glycol di-methacrylate, aliphatic polyurethane di-acrylates, polyurethane di-methacrylates, butanediol di-methacrylate (BDDMA), and any derivative or combination thereof.

[062] Further non-limiting examples of cross-linkers are trimethylolpropane trimethacrylate (TMPTMA), trimethylolpropane triacrylate (TMPTA), pentaerythritol tetraacrylate, dipentaerithritol hexaacrylate, multi-functional dendritic acrylates and methacrylates having three or more functional groups, and any derivative or combination thereof.

[063] In some embodiments, the term, “crosslinked” and/or “crosslinking”, as used herein, and any grammatical derivative thereof refers generally to a chemical process or the corresponding product thereof in which two chains of polymeric molecules are attached by bridges, a "cross-linker", composed of an element, a group or a compound, which join certain carbon atoms of the chains by primary chemical. Therefore, the general properties of a cross-linker compound, include: having bi- or poly-functional groups enabling attachment to at least two moieties.

[064] In some embodiments, the cross-linker has a di-functional groups. In some embodiments, the cross-linker has a tri-functional groups. In some embodiments, the cross-linker is characterized by having more than one, or in some embodiments, two

functional groups. This enables, e.g., the attachment of the cross-linker to at least three monomeric units.

[065] In some embodiments, the cross-linked polymer concentration is in the range of from about 5% to about 25%, by weight of the composite. In some embodiments, the cross-linked polymer concentration is in the range of from about 10% to about 25%, by weight of the composite. In some embodiments, the cross-linked polymer concentration is in the range of from about 5% to about 30%, by weight of the composite. In some embodiments, the cross-linked polymer concentration is in the range of from about 10% to about 30%, by weight of the composite. In some embodiments, the cross-linked polymer concentration is in the range of from about 7% to about 20%, by weight of the composite. In some embodiments, the cross-linked polymer concentration is in the range of from about 7% to about 25%, by weight of the composite. In some embodiments, the composite comprises 10%, by weight of cross-linked polymer.

[066] In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:100 to 1:2, respectively. In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:50 to 1:10, respectively. In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:120 to 1:1, respectively. In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:50 to 1:2, respectively. In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:100 to 1:10, respectively. In some embodiments, the ratio of the polymeric backbone and one or more cross-linkers is from 1:100 to 1:1, respectively.

[067] In some embodiments, the cross-linked polymer comprises less than 30%, less than 25%, less than 20%, less than 15%, less than 10%, less than 5%, less than 2%, or less than 1%, by weight, of one or more cross-linkers. In some embodiments, the cross-linked polymer comprises from 1% to 20%, by weight, of one or more cross-linkers. In some embodiments, the cross-linked polymer comprises from 0.05% to 30%, by weight, of one or more cross-linkers. In some embodiments, the cross-linked polymer comprises from 1% to 30%, by weight, of one or more cross-linkers.

[068] In some embodiments, the composite comprises less than 70%, less than 75%, less than 80%, less than 85%, less than 90%, less than 91%, less than 92%, less than 93%, or less than 95%, by weight, of mineral. In some embodiments, the mineral is in

the range of from 75% to 93%, by weight, of the composite. In some embodiments, the mineral is in the range of from 70% to 93%, by weight, of the composite. In some embodiments, the mineral is in the range of from 70% to 90%, by weight, of the composite. In some embodiments, the mineral is in the range of from 75% to 90%, by weight, of the composite. In some embodiments, the mineral is in the range of from 80% to 90%, by weight, of the composite. In some embodiments, the mineral is in the range of from 85% to 95%, by weight, of the composite. In some embodiments, the mineral is in the range of from 85% to 93%, by weight, of the composite. In some embodiments, the composite comprises 90% of at least one mineral.

[069] In some embodiments, the composite comprises less than 1%, less than 0.5% or less than 0.1% of styrene (e.g., as a free styrene or in the form of a monomeric unit). In some embodiments, the composite is devoid of styrene.

[070] In some embodiments, the composite comprises less than 1%, less than 0.5% or less than 0.1%, or less than 0.01%, of heavy metals. In some embodiments, the composite is devoid of heavy metals (e.g., cobalt). In some embodiments, by "heavy metals" it is meant to refer to transition metals.

[071] In some embodiments, the composite is characterized by glass-transition temperature (T_g) in the range of from 60°C to 120°C. In some embodiments, the composite is characterized by T_g in the range of from 65°C to 110°C. In some embodiments, the composite is characterized by T_g in the range of from 75°C to 95°C. In some embodiments, the composite is characterized by T_g in the range of from 75°C to 110°C. In some embodiments, the composite is characterized by T_g in the range of from 65°C to 95°C. In some embodiments, the composite is characterized by T_g in the range of from 70°C to 110°C. In some embodiments, the composite is characterized by T_g in the range of from 70°C to 100°C.

[072] In some embodiments, the composite is characterized by young modulus in the range of from 10,000 to 30,000 MPa. In some embodiments, the composite is characterized by young modulus in the range of from 13,000 to 30,000 MPa. In some embodiments, the composite is characterized by young modulus in the range of from 16,000 to 25,000 MPa. In some embodiments, the composite is characterized by young modulus in the range of from 15,000 to 25,000 MPa. In some embodiments, the composite is characterized by young modulus in the range of from 10,000 to 25,000

MPa. In some embodiments, the composite is characterized by young modulus in the range of from 15,000 to 30,000 MPa.

[073] In some embodiments, the composite is characterized by flexural strength in the range of from 40 to 110 MPa. In some embodiments, the composite is characterized by flexural strength in the range of from 50 to 110 MPa. In some embodiments, the composite is characterized by a flexural strength in the range of from 55 to 110 MPa. In some embodiments, the composite is characterized by a flexural strength in the range of from 60 to 95 MPa. In some embodiments, the composite is characterized by a flexural strength in the range of from 50 to 120 MPa. In some embodiments, the composite is characterized by a flexural strength in the range of from 60 to 110 MPa. In some embodiments, the composite is characterized by flexural strength in the range of from 60 to 100 MPa. In some embodiments, the composite is characterized by flexural strength in the range of from 50 to 95 MPa.

[074] In some embodiments, the composite is characterized by toughness (G_{1c}) of at least 30 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) of at least 20 J/m^2, at least 25 J/m^2, at least 30 J/m^2, at least 40 J/m^2, at least 45 J/m^2, at least 50 J/m^2, or at least 55 J/m^2.

[075] In some embodiments, the composite is characterized by toughness (G_{1c}) of less than 150 J/m^2, less than 140 J/m^2, less than 120 J/m^2, less than 110 J/m^2, less than 100 J/m^2, less than 95 J/m^2, less than 90 J/m^2, less than 85 J/m^2, or less than 150 J/m^2.

[076] In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from 30 to 100 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from 45 to 100 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from J/55 to 100 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from 30 to 110 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from 45 to 110 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of from 55 to 110 J/m^2. In some embodiments, the composite is characterized by toughness (G_{1c}) in the range of 45 to 120 J/m^2.

[077] In some embodiments, the composite is characterized by heat distortion temperature (HDT) of at least 35°C, at least 45°C, at least 55°C, at least 65°C, at least

70°C or at least 75°C. In some embodiments, the composite is characterized by HDT in the range of from 55°C to 110°C. In some embodiments, the composite is characterized by HDT in the range of from 65°C to 110°C. In some embodiments, the composite is characterized by HDT in the range of from 55°C to 100°C. In some embodiments, the composite is characterized by HDT in the range of from 65°C to 100°C.

[078] In some embodiments, the composite is characterized by whiteness index change (ΔWI) of less than 55%, less than 45%, less than 35%, less than 25%, less than 15% or less than 5% after 50-200 hours of radiation exposure in a defined range of KLy.

[079] In some embodiments, the composite is characterized by a yellowness index change (ΔYI) of less than 75%, less than 65%, less than 55%, less than 45%, less than 35%, less than 25%, less than 15% or less than 5% after 50-200 hours of radiation exposure in a defined range of KLy.

[080] In some embodiments, by "radiation exposure" it is meant to refer to UV radiation exposure, as defined hereinthroughout (e.g., UVA or UVB).

[081] In some embodiments, the composite comprises an additive e.g., a toughener. In some embodiments, the toughener is attached to the cross-linked polymer.

[082] In some embodiments, the toughener is characterized by a predetermined particle size and amount in the composition.

[083] In some embodiments, the toughener is made of one or more graft polymers.

[084] Typically, but not exclusively, graft polymers are methacrylate/butadiene-styrene polymers, acrylate-methacrylatelbutadiene-styrene polymers, or acrylonitrile/butadiene-styrene polymers.

[085] In some embodiments, the toughener is selected from, without being limited thereto, polyurethanes mono acrylate, polyurethanes diacrylate, polyurethanes triacrylate, or any combination thereof.

[086] In some embodiments, the toughener is in the form of a core/shell structure.

[087] Typically, but not exclusively, core/shell polymers have a soft core of an elastomeric material. In some embodiments, the core/shell polymers normally have a soft core of an elastomeric material containing graft polymers known to those skilled in the art as rubber tougheners. In some embodiments, the core/shell polymeric toughener is phase separated from the acrylic based polymers.

[088] The term "elastomer" has a common meaning in the art, and, in some embodiments, refers to a synthetic rubber, plastic or other polymer which can be stretched to at least twice its original length then return to its original shape with force.

[089] In some embodiments, the shell comprises grafted polymeric material which contains no reactive groups. In some embodiments, the core/shell polymer may also be a so-called multi-core/shell polymer, conveniently one having the structure soft core, hard shell, soft shell and hard shell.

[090] Non-limiting examples of elastomers which may be used as a core material are polybutadiene, polyacrylates and polymethacrylates and their co- or terpolymers with polystyrene, polyacrylonitrile or polysulfide.

[091] In some embodiments, the core comprises polybutadiene or polybutylacrylate.

[092] In exemplary embodiments, the core comprises an elastomer comprising a styrene butadiene or a polymer thereof. In further exemplary embodiments, the core comprises an elastomer comprising a silicone or a polymer thereof.

[093] Non-limiting examples of polymeric shell materials are polystyrene, polymethyl methacrylate, polyacrylonitrile, polyacrylate and polymethacrylate mono-, co- or terpolymers or styrene/acrylonitrile/glycidyl methacrylate terpolymers.

[094] In some embodiments, the cross-linked polymer has attached thereto less than 1%, less than 2%, or less than 5% of toughener, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 0.1% to 30%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 1% to 30%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 0.1% to 25%, by weight. In some embodiments, the cross-linked polymer comprises a toughener in the range of from 0.1% to 20%, by weight. In some embodiments, the cross-linked polymer comprises a toughener in the range of from 1% to 25%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 1% to 20%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 2% to 20%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 2% to 25%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 2% to 30%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of

from 3% to 20%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 3% to 15%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 3% to 10%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 3% to 25%, by weight. In some embodiments, the cross-linked polymer has attached thereto a toughener in the range of from 3% to 30%, by weight.

[095] In some embodiments, the composite further comprises a linker (also referred to as "binder"). In some embodiments, the linker is configured to contact inorganic materials such as the mineral. In some embodiments, the linker is associated (e.g., physically attached or adsorbed) to the polymeric backbone and to at least one mineral.

[096] In some embodiments, the linker is covalently attached to a monomeric unit of the polymeric backbone. In some embodiments, the linker is derived from acryloyl.

[097] Hereinthroughout, the terms “associated”, “linked” (in distinction from "cross-linker"), and any grammatical derivative thereof, which are used herein interchangeably, describe a linkage between the organic and inorganic materials (e.g., inorganic mineral and organic polymer), carried out and/or facilitated by using linker molecules, wherein the linkage may be covalent in a non-limiting fashion.

[098] In some embodiments, the linker is selected from, but is not limited to, alkoxysilane, or any derivative thereof.

[099] In some embodiments, the composite comprises a linker in the range of from 0.01% to 0.5%, including any value therebetween, by weight (of the total composite). In some embodiments, the composite comprises a linker in the range of from 0.01% to 0.3%, including any value therebetween, by weight. In some embodiments, the composite comprises a linker in the range of from 0.02% to 0.5%, including any value therebetween, by weight. In some embodiments, the composite comprises a linker in the range of from 0.02% to 0.3%, including any value therebetween, by total weight. In some embodiments, the composite comprises a linker in the range of from 0.01% to 1%, including any value therebetween, by weight. In some embodiments, the composite comprises a linker in the range of from 0.05% to 0.15%, including any value therebetween, by total weight.

The process

[0100] According to another aspect of some embodiments of the present invention, there is provided a method for obtaining a composition comprising a composite made of a cross-linked polymer and a mineral.

[0101] In some embodiments, the method comprises the steps of:

a. mixing a plurality of monomers, at least one cross-linker, a peroxide initiator, and optionally at least one toughener and one or more polymer stabilizers, thereby obtaining a mixture of the cross-linked polymer;

b. adding a mineral to the mixture;

c. curing the mixture at a temperature above 90°C.

[0102] In some embodiments, the cross-linked polymer is obtained by mixing a polymeric backbone, at least one cross-linker, a least one initiator, and optionally at least one toughener and one or more polymer stabilizers.

[0103] In some embodiments, the polymer stabilizer comprises a quinone, a phenol, an amine, or any combination thereof.

[0104] In some embodiments, the cross-linked polymer is obtained by mixing a polymeric backbone, at least one cross-linker, and at least one toughener. In some embodiments, the cross-linked polymer is obtained by mixing a polymeric backbone and at least one cross-linker.

[0105] Embodiments of the monomers (and the monomeric units), cross-linkers, toughener, peroxide initiators and one or more polymer stabilizers are described hereinthroughout.

[0106] In some embodiments, the method comprises a further step prior to the curing step, of pouring the compounds mixture (e.g., the monomers, the cross-linker, the peroxide initiator) to a support or a temporary support.

[0107] Non-limiting examples of support are rubbers, papers, plastic or any other polymeric material, silicon sheet or the like with or without a support frame or a shaping frame, and a mold, such as a rubber tray mold.

[0108] In some embodiments, the terms “cure”, "curing", and any grammatical derivative thereof, which are used herein interchangeably, a change in the physical

properties of a material by chemical reaction through condensation, polymerization or vulcanization. Usually accomplished by the action of heat and catalysts, alone or in combination with or without pressure.

[0109] In some embodiments, prior to the curing step, the mixture is poured into a mold in the form of a desired slab (e.g., at a size of 400 cm × 200 cm × 3 cm with or without wall shaping). In some embodiments, prior to the curing step, the mixture is compacted by a vacuum and/or vibration. In some embodiments, the vibro-compression is performed at high pressure, e.g., about 100 tons.

[0110] In some embodiments, the curing step further comprises a step of adding a linker to the curing process.

[0111] In some embodiments, the method further comprises a step of adding suitable amounts of various additives. These additives may include, for example, colorants, dyes, pigments, chemical reagents, antimicrobial substances, fungicidal agents, or the like, or any combination thereof. In some embodiments, the additive is added to the curing process. In some embodiments, the additive may be added to the mixture at various stages of production (e.g., addition to the blending of raw materials).

[0112] In some embodiments, the additive may be present in the final composition, (also referred to as the "stone product"). In some embodiments, the additive may further determine various characteristics of the final composition. Such characteristics may include physical properties, such as: color, texture, display pattern, and the like; chemical properties, such as, for example, chemical resistance, pH properties, and the like; biological properties, such as, for example, antibacterial properties, and the like; and/or mechanical properties, such as, for example, toughness, flexural strength, scratch resistance, impact resistance, or the like.

[0113] In some embodiments, the term “colorant” may include dyes, pigments, colorants, and the like, or any combination thereof in any form, such as liquid, paste, fluid, or the like.

[0114] In some embodiments, the curing step is performed at a temperature (referred to as: "curing temperature") of above 70°C, above 80°C, above 90°C, above 95°C, above 100°C or above 110°C. In some embodiments, the curing temperature is less than 130°C, less than 120°C, less than 115°C, less than 110°C, less than 105°C, less than 100°C, less than 95°C or less than 90°C.

[0115] In some embodiments, the curing temperature is in the range of 70°C to 130°C. In some embodiments, the curing temperature is in the range of from 80°C to 130°C. In some embodiments, the curing temperature is in the range of from 90°C to 130°C. In some embodiments, the curing temperature is in the range of from 70°C to 120°C. In some embodiments, the curing temperature is in the range of from 80°C to 120°C. In some embodiments, the curing temperature is in the range of from 90°C to 120°C. In some embodiments, the curing temperature is in the range of from 95°C to 120°C. In some embodiments, the curing temperature is in the range of from 70°C to 110°C. In some embodiments, the curing temperature is in the range of from 80°C to 110°C. In some embodiments, the curing temperature is in the range of from 90°C to 110°C. In some embodiments, the curing temperature is in the range of from 95°C to 110°C. In some embodiments, the curing temperature is in the range of from 95°C to 105°C.

[0116] In some embodiments, the curing is performed at time duration of (referred to as "curing duration time") at least 20, at least 25, at least 30, at least 35, at least 40, at least 45, at least 50, at least 55 or at least 60 minutes. In some embodiments, the curing is performed at time duration of less than 40, less than 45, less than 50, less than 55, less than 60, less than 70, less than 90, or less than 120 minutes.

[0117] In some embodiments, the curing duration time is from 20 to 90 minutes. In some embodiments, the curing duration time is from 20 to 70 minutes. In some embodiments, the curing duration time is from 20 to 45 minutes. In some embodiments, the curing duration time is from 30 to 90 minutes. In some embodiments, the curing duration time is from 30 to 70 minutes. In some embodiments, the curing duration time is from 30 to 60 minutes. In some embodiments, the curing duration time is from 30 to 45 minutes.

[0118] In some embodiments, the peroxide initiator is selected from, but is not limited to: di-benzoyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, cyclohexanone peroxide, methylethyl peroxide, tert-butyl peroxyoctoate, tert-butyl peroxybenzoate, dicumyl peroxide, 1,1-bis(tert-butyl peroxy)3,3,5-trimethylcyclohexane, tert-butyl peroxymaleate, and any derivative or combination thereof.

Definitions

[0119] The term “composite”, is used herein to denote that the composition is made of at least two components, namely, made of non-pristine substances. In some

embodiments, the two or more substances have different characteristics and in each substance, retains its identity while contributing desirable properties to the whole.

[0120] Herein, the term "monomer" refers to a molecule that may bind chemically to other molecules to form a polymer.

[0121] The terms "monometric unit" refer to the repeat units, derived from the corresponding monomer. The polymer comprises the monomeric units. By "derived from" it is meant to refer to the compound following the polymerization process.

[0122] As used herein, the term "polymer" describes an organic substance composed of a plurality of repeating structural units (monomeric units) covalently connected to one another.

[0123] As used herein, “polymer backbone” generally refers to a polymer comprising monomeric units. It is to be understood that in the context of the present invention, the term “polymeric backbone” refers to the main chain of polymeric skeleton together with chain branches projecting from the polymeric skeleton. The branches may comprise one or more of either A1 and/or A2 monomeric units as described herein.

[0124] The term "peroxide initiator" or "radical" refers to free radical building block(s) that can initiate polymerization. Since the initiator can generate a radical by abstracting hydrogen from a carbon-hydrogen bond, when it is used in combination with an organic material, such as a polymer, a chemical bond can be formed. Following creation of free radical monomeric units, polymer chains grow rapidly with successive addition of building blocks onto free radical sites.

[0125] The following water soluble exemplary initiators may be used, without being limited thereto: peroxides such as ammonium persulfate, potassium persulfate, sodium persulfate, hydrogen peroxide, benzoyl peroxide, cumene hydroperoxide, or di-t-butyl peroxide; a redox initiator that is a combination of the above-mentioned peroxide and a reducing agent such as a sulfite, a bisulfite, thiosulfate, formamidinesulfinic acid, or ascorbic acid; or an azo-based radical polymerization initiator, such as, without limitation, 2,2'-azobis(2-amidinopropane) (AIBN), AIBNCOOH, and 2,2'-azobis(2-amidinopropane), and potassium persulfate (PPS), or any combination thereof.

[0126] Further embodiments of the initiator are described hereinthroughout.

[0127] The term "ultraviolet (UV) light" is electromagnetic radiation with a wavelength shorter than that of visible light, but longer than X-rays, in the range 10 nm to 400 nm, and energies from 3eV to 124 eV. The spectrum consists of electromagnetic waves with frequencies higher than those that humans identify as the color violet. UVA: 315-400 nm and UVB: 280-315 nm.

[0128] In some embodiments, the size of the particles described herein represents an average size, or in some embodiments, a median size of a plurality of particle composites or particles.

[0129] As referred to herein, the terms "slab", "artificial marble", "engineered stone" and "quartz surfaces" may interchangeably be used. Thus, when referencing any of the terms "slab", "artificial marble", "engineered stone" and "quartz surfaces", it implies that all the terms are covered.

[0130] In some embodiments, the term "polymer stabilizer", or "stabilizer" refers to a polymer having a function that prevents oxidation, free radical formation and cross-linking reactions during polymerization.

[0131] As used herein, the term "alkyl" describes an aliphatic hydrocarbon including straight chain and branched chain groups. Preferably, the alkyl group has 21 to 100 carbon atoms, and more preferably 21-50 carbon atoms. Whenever a numerical range; e.g., “21-100”, is stated herein, it implies that the group, in this case the alkyl group, may contain 21 carbon atom, 22 carbon atoms, 23 carbon atoms, etc., up to and including 100 carbon atoms. In the context of the present invention, a "long alkyl" is an alkyl having at least 20 carbon atoms in its main chain (the longest path of continuous covalently attached atoms). A short alkyl therefore has 20 or less main-chain carbons. The alkyl can be substituted or unsubstituted, as defined herein.

[0132] The term "alkyl", as used herein, also encompasses saturated or unsaturated hydrocarbon, hence this term further encompasses alkenyl and alkynyl.

[0133] The term "alkenyl" describes an unsaturated alkyl, as defined herein, having at least two carbon atoms and at least one carbon-carbon double bond. The alkenyl may be substituted or unsubstituted by one or more substituents, as described hereinabove.

[0134] The term "alkynyl", as defined herein, is an unsaturated alkyl having at least two carbon atoms and at least one carbon-carbon triple bond. The alkynyl may be substituted or unsubstituted by one or more substituents, as described hereinabove.

[0135] The term "cycloalkyl" describes an all-carbon monocyclic or fused ring (i.e., rings which share an adjacent pair of carbon atoms) group where one or more of the rings does not have a completely conjugated pi-electron system. The cycloalkyl group may be substituted or unsubstituted, as indicated herein.

[0136] The term "aryl" describes an all-carbon monocyclic or fused-ring polycyclic (i.e., rings which share adjacent pairs of carbon atoms) groups having a completely conjugated pi-electron system. The aryl group may be substituted or unsubstituted, as indicated herein.

[0137] The term "alkoxy" describes both an -O-alkyl and an -O-cycloalkyl group, as defined herein.

[0138] The term "aryloxy" describes an -O-aryl, as defined herein.

[0139] Each of the alkyl, cycloalkyl and aryl groups in the general formulas herein may be substituted by one or more substituents, whereby each substituent group can independently be, for example, halide, alkyl, alkoxy, cycloalkyl, alkoxy, nitro, amine, hydroxyl, thiol, thioalkoxy, thiohydroxy, carboxy, amide, aryl and aryloxy, depending on the substituted group and its position in the molecule. Additional substituents are also contemplated.

[0140] The term "acryloyl" describes a H2C=CH-C(=O)-R' group, where R' is as defined herein.

[0141] The term "halide", "halogen" or “halo” describes fluorine, chlorine, bromine or iodine.

[0142] The term “haloalkyl” describes an alkyl group as defined herein, further substituted by one or more halide(s).

[0143] The term “haloalkoxy” describes an alkoxy group as defined herein, further substituted by one or more halide(s).

[0144] The term “hydroxyl” or "hydroxy" describes a –OH group.

[0145] The term "thiohydroxy" or “thiol” describes a -SH group.

[0146] The term "thioalkoxy" describes both an -S-alkyl group, and a -S-cycloalkyl group, as defined herein.

[0147] The term "thioaryloxy" describes both an -S-aryl and a -S-heteroaryl group, as defined herein.

[0148] The term "amine" describes a –NR'R'' group, with R' and R'' as described herein.

[0149] The term "heteroaryl" describes a monocyclic or fused ring (i.e., rings which share an adjacent pair of atoms) group having in the ring(s) one or more atoms, such as, for example, nitrogen, oxygen and sulfur and, in addition, having a completely conjugated pi-electron system. Examples, without limitation, of heteroaryl groups include pyrrole, furane, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrimidine, quinoline, isoquinoline and purine.

[0150] The term "heteroalicyclic" or "heterocyclyl" describes a monocyclic or fused ring group having in the ring(s) one or more atoms such as nitrogen, oxygen and sulfur. The rings may also have one or more double bonds. However, the rings do not have a completely conjugated pi-electron system. Representative examples are piperidine, piperazine, tetrahydrofurane, tetrahydropyrane, morpholino and the like.

[0151] The term "carboxy" or "carboxylate" describes a -C(=O)-OR' group, where R' is hydrogen, alkyl, cycloalkyl, alkenyl, aryl, heteroaryl (bonded through a ring carbon) or heteroalicyclic (bonded through a ring carbon) as defined herein.

[0152] The term "carbonyl" describes a –C(=O)-R' group, where R' is as defined hereinabove.

[0153] The above-terms also encompass thio-derivatives thereof (thiocarboxy and thiocarbonyl).

[0154] The term "thiocarbonyl" describes a –C(=S)-R' group, where R' is as defined hereinabove.

[0155] A "thiocarboxy" group describes a -C(=S)-OR' group, where R' is as defined herein.

[0156] A "sulfinyl" group describes an -S(=O)-R' group, where R' is as defined herein.

[0157] A "sulfonyl" or "sulfonate" group describes an -S(=O)2-R' group, where Rx is as defined herein.

[0158] A "carbamyl" or "carbamate" group describes an -OC(=O)-NR'R" group, where R' is as defined herein and R" is as defined for R'.

[0159] A "nitro" group refers to a -NO2 group.

[0160] A "cyano" or "nitrile" group refers to a -C≡N group.

[0161] As used herein, the term "azide" refers to a –N3 group.

[0162] The term "sulfonamide" refers to a -S(=O)2-NR'R" group, with R' and R" as defined herein.

[0163] The term "phosphonyl" or "phosphonate" describes an -O-P(=O)(OR')2 group, with R' as defined hereinabove.

[0164] The term "phosphinyl" describes a –PR'R" group, with R' and R" as defined hereinabove.

[0165] The term "alkaryl" describes an alkyl, as defined herein, which substituted by an aryl, as described herein. An exemplary alkaryl is benzyl.

[0166] The term "heteroaryl" describes a monocyclic or fused ring (i.e., rings which share an adjacent pair of atoms) group having in the ring(s) one or more atoms, such as, for example, nitrogen, oxygen and sulfur and, in addition, having a completely conjugated pi-electron system. Examples, without limitation, of heteroaryl groups include pyrrole, furane, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrimidine, quinoline, isoquinoline and purine. The heteroaryl group may be substituted or unsubstituted by one or more substituents, as described hereinabove. Representative examples are thiadiazole, pyridine, pyrrole, oxazole, indole, purine and the like.

[0167] As used herein, the terms "halo" and "halide", which are referred to herein interchangeably, describe an atom of a halogen, that is fluorine, chlorine, bromine or iodine, also referred to herein as fluoride, chloride, bromide and iodide.

[0168] The term "haloalkyl" describes an alkyl group as defined above, further substituted by one or more halide(s).

General

[0169] As used herein the term "about" refers to ± 10 %.

[0170] The terms "comprises", "comprising", "includes", "including", “having” and their conjugates mean "including but not limited to". The term “consisting of” means “including and limited to”. The term "consisting essentially of" means that the composition, method or structure may include additional ingredients, steps and/or parts, but only if the additional ingredients, steps and/or parts do not materially alter the basic and novel characteristics of the claimed composition, method or structure.

[0171] The word “exemplary” is used herein to mean “serving as an example, instance or illustration”. Any embodiment described as “exemplary” is not necessarily to be construed as preferred or advantageous over other embodiments and/or to exclude the incorporation of features from other embodiments.

[0172] The word “optionally” is used herein to mean “is provided in some embodiments and not provided in other embodiments”. Any particular embodiment of the invention may include a plurality of “optional” features unless such features conflict.

[0173] As used herein, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise. For example, the term "a compound" or "at least one compound" may include a plurality of compounds, including mixtures thereof.

[0174] Throughout this application, various embodiments of this invention may be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0175] Whenever a numerical range is indicated herein, it is meant to include any cited numeral (fractional or integral) within the indicated range. The phrases “ranging/ranges between” a first indicate number and a second indicate number and “ranging/ranges from” a first indicate number “to” a second indicate number are used herein

interchangeably and are meant to include the first and second indicated numbers and all the fractional and integral numerals therebetween.

[0176] As used herein the term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by practitioners of the chemical, and material arts.

[0177] As used herein, the term “treating” includes abrogating, substantially inhibiting, slowing or reversing the progression of a condition, of aesthetical symptoms of a condition.

[0178] In those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0179] It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable subcombination or as suitable in any other described embodiment of the invention. Certain features described in the context of various embodiments are not to be considered essential features of those embodiments, unless the embodiment is inoperative without those elements.

[0180] Various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below find experimental support in the following examples.

EXAMPLES

[0181] Reference is now made to the following examples which, together with the above descriptions, illustrate the invention in a non-limiting fashion.

Methods

[0182] Composites were examined under spectrophotometer in order to characterize their whiteness index (WI) after 100 or 200 hours with intervals of 6 hours irradiation of UV-A/UV-B light and 6 hours under darkness and moisture conditions. UV experiments were done by QUV-machine on sample dimensions of 7*15 cm with a distance of 50 mm between the lamp and the sample.

[0183] Young modulus and flexural strength were tested by using Lloyd device, load cell of 10 kN, sample size of 20x10x150 mm and bar speed of 10 mm/min according to an internal standard based on the Israeli standard 4491.

[0184] Crack propagation (ΔG) in was examined by a procedure based on ASTM 1421-6 with sample size of 1700x40x20 mm and crack initial length of 20 mm located in the middle of the sample.

[0185] Glass transition temperature (Tg) and Heat deflection temperature (HDT) were measured using DMA technique.

EXAMPLE 1

Materials and Methods

[0186] Nine different composites were examined, comprising 10% of cross-linked polymer and 90% of quartz particles, in order to characterize their flexural strength, young modulus, G_{1c} and heat distortion temperature (HDT).

[0187] As shown in **Table 1**, these samples contain:

- 3 types of acrylic mono-functional monomers: (i) 0.3% of methyl-methacrylate (MMA), (ii) n-butyl acrylate (n-BA) and (iii) 2-ethylhexyl acrylate (2EHA);
- 3 types of quartz particles with diameter of: (i) 0.2-0.5 mm, (ii) 0.06-0.2 mm; and (iii) 0.001-0.05 mm;
- 0.02% of tri-ethylene glycol di-methacrylate (cross-linker);
- 0.12% of a linker comprising methoxysilane;
- Di-benzoyl peroxide (DBP) initiator;

- 2,6-di-tert-butyl-4-methylphenol (TBP);
- Core-shell toughener (XT-100 from Arkema Inc.);

Table 1

Num	Quartz particles				Cross-linked polymer							
	Percentage in composite (%)	Type 1 (%)	Type 2 (%)	Type 3 (%)	Percentage in composite (%)	MMA (%) T_g=	n-BA (%) T_g=	2EHA (%) T_g=	Toughener (%)	DBP (%)	TBP (%)	Curing time at 100°C (min)
1	90	50	10	40	10	80	0	20	5	0.1	0.01	40
2	90	50	10	40	10	80	10	10	5	0.1	0.01	40
3	90	50	10	40	10	80	0	20	5	0.28	0.00	25
4	90	50	10	40	10	80	0	20	5	0.15	0.04	70
5	90	50	10	40	10	60	20	20	5	0.1	0.01	40
6	90	70	30	10	10	80	0	20	5	0.1	0.01	40
7	90	50	10	40	10	80	0	20	15	0.1	0.01	40
8	85	50	10	40	15	80	10	10	5	0.15	0.015	45
9	90	50	10	40	10	80	10	10	5	0.04	0.01	85

The curing was at temperature of 100 °C for 25-85 minutes.

Results

[0188] The results are summarized in Table 2 below:

Table 2

Number of sample	Flexural Strength (MPa)	Young Modulus (MPa)	G_{1c} (J/m^2)	HDT (^0C)	Testing results	Remarks
1	85	19000	65	85	Passed	
2	88	19500	60	88	Passed	
3	43	10000	15	82	Not passed	Inferior results for cracks formation
4	72	17000	67	78	Not passed	Too long curing time
5	80	14500	70	55	Not passed	Soft - low HDT
6	50	12000	25	70	Not passed	Not optimal distribution of varied sizes of quartz particles. Not homogeneous distribution in the cross-linked polymer. Micro- cracks formation in slab bulk

						during shrinkage of cross-linked polymer.
7	55	11500	75	68	Not passed	Too low young modulus
8	70	16000	42	80	Passed	
9	78	17500	45	75	Not passed	Too long curing time because of not optimal concentration of peroxide and too high concentration of radical.

[0189] The composite was distorted and smelly, when 11.85% of cross-linked polymer instead of 10% was cured with quartz particles.

EXAMPLE 2

Materials and Methods

[0190] As shown in **Table 3**, different compositions of cross-linked polymer were characterized by T_g (loss modulus), young modulus, flexural strength at max loading (as described above), ΔG, G_{1c}, $\Delta G + G_{1c}$, and UV-stability including whiteness index (WI) (as described above).

Table 3

Number of sample	MMA (%)	n-BA (%)	2EHA (%)	Toughener (%)	Curing time (min)	Curing temp. (°C)	Additional materials
1	85	0	15		60	90/120	
2	80	0	20		30	120	
3	80	0	20		60	95	
4	80	0	20		40	95	
5	80	0	20		40	100	
6	80	0	20		40	100	Peroxide paste
7	80	0	20			100	
8	80		20		40	100	white pigment
9	80	0	20	10	40	100	20% PMMA
10	60	20	20		40	100	
11	80	0	20	5	45	100	20% PMMA
12	70	15	15		45	100	
13	70	15	15		45	100	4% Cross linker
14	80	0	20		45	100	4% Cross linker and white pigment
15	80	0	20		35	100	1.2% Peroxide paste
16	80	0	20		45	100	1.5% Peroxide paste
17	80	0	20		45	100	3% Cross linker and white pigment

18	80	0	20		45	100	2% Cross linker and white pigment
19	70	15 n-BMA	15		49	100	
20	70	15 n-BMA	15	5	45	100	

Table 4

Number of sample	HDT (°C)	$\Delta G + G_{1c}$ (kJ/m^2)	G_{1c} (kJ/m^2)	ΔG (kJ/m^2)	Flexural strength (MPa)	Young modulus (MPa)	T_g (°C)
1		35	28	10.6	64	24,184	92
2		76	53	12.6	80	23,351	79
3		66	62	4.2	76	22,264	78
4		57	55	1.8	70	22,910	80
5		66	69	7.9	78	22,443	79
6		57	40	10.9	51	18,707	66
7		142	96	46.4	81	20,459	77
8	79	80	58	22.0	65	20,033	83
9	82	153	91	61.8	83	19,703	83
10	52	73	55	18.2	56	15,477	47
11	84	119	97	22.1	82	21,670	84
12	71	91	78	13.5	75	20,724	64
13	88	69	55	13.7	75	24,126	84
14	78	72	59	13.3	73	23,539	70
15	84	80	62	18.3	79	23,875	84

16	85	85	66	18.4	75	23,469	83
17	83	84	67	16.5	78	22,818	81
18	84	74	60	13.7	79	23,194	81
19	77	81	64	17.8	80	22,631	76
20	78	107	81	26.2	81	20,824	78

[0191] These samples contain:

- The polymeric backbone comprises 3 types of acrylic mono-functional monomers: (i) 0.3% of methyl-methacrylate (MMA), (ii) n-butyl acrylate (n-BA) and (iii) 2-ethylhexyl acrylate (2EHA);
- Core-shell toughener (XT-100 or Durastrength 480 from Arkema Inc.) Di-benzoyl peroxide paste (Luperox 75, Luperox ANS50, Perkadox 16 or Paradox L40RPS from Arkema Inc.)
- Triethylene glycol dimethacrylate - cross-linker (SR-205 from Arkema Inc.)
- White pigment powder or white pigment paste (titan premix, white paste P1823, white paste 9660PU/WE-6-NM or BYK-S782 from Florma)
- Poly methyl methacrylate (PMMA)
- Polyurethane resin (G4230/G4267 by Rahn)

Table 5 below presents the results of whiteness tests:

Table 5

	UVA		**UVB**	
	100 hrs.	**200 hrs.**	**100 hrs.**	**200 hrs.**
Number of sample	**ΔWI (%)**	**ΔWI (%)**	**ΔWI (%)**	**ΔWI (%)**
1	-0.25	-1.0	-4.0	-5.4
2	-1.17	-1.6	-4.0	-4.4
3	0.36		-6.4	-7.3
4	-1.96		-3.9	-6.6
5	0.16	-0.3	-3.0	-2.1
6	1.85	2.5	-5.1	-9.9
7	-0.23	-4.8	-8.8	-10.5
8	-1.71	-2.1	-9.5	-10.6
9	-3.61	-3.8	-7.7	-10.3
10	-2.35	-2.1	-6.4	-8.0

11	-2.64		-9.2	-9.3
12	-1.46		-6.6	-7.2
13	-3.01	-2.2	-4.8	-5.4
14	-0.78	-1.0	-5.7	-4.9
15	-0.81	-0.6	-5.4	-6.7
16	0.87	0.7	-3.6	-3.4
17	1.24	0.6	-5.6	-6.6
18	-0.64	-1.1	-5.5	-6.3
19	0.73	1.2	-6.0	-6.9
20	-0.85	-2.7	-7.5	-8.0

[0192] As shown in **Table 6**, the acrylic slab has better UV-stability than the polyester slab. Thus, polyester degradation is faster than the acrylic polymer.

Table 6

	UVA		**UVB**	
	100 hrs.	**200 hrs.**	**100 hrs.**	**200 hrs.**
	ΔWI (%)	**ΔWI (%)**	**ΔWI (%)**	**ΔWI (%)**
Acrylic slab	0.2-3%	4-12%	3-12%	4-15%
Polyester slab	1.3-3%	N.A	70-80%	100-110%

[0193] In exemplary procedures, the cross-linking density was calculated, assuming all double bonds of a monomer with two or more double bonds have been reacted.

[0194] For example: using SR 205 (di-acrylate); Mw = 286 g/mole, and a concentration of about 2% (= 20 g/l) of the binder gives 2 x 20/286 = 0.14 moles of double bonds/l.

[0195] It is assumed that the binder concentration is about 10% in an engineered stone which gives an exemplary concentration of cross-links of about 0.014 mole/l.

[0196] Using Avogadro number = 6.0×10^{23} units/mole, the cross-linking density can be assessed in terms of 8.4×10^{21} units/l.

[0197] In case of high molecular weight cross-linkers (e.g. polyurethane-di-acrylates) but lower concentration, cross-linking density can be lower.

[0198] In further exemplary procedures, cross-linking density is lower (e.g., $2x10^{20}$ units/l), in case of acrylate cross-linkers with higher amount of double bonds (e.g., up to 20 double bonds) in their structure, depends on the concentration of the cross-linker.

[0199] Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

[0200] All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention. To the extent that section headings are used, they should not be construed as necessarily limiting.

WHAT IS CLAIMED IS:

1. A composition comprising a composite, said composite comprising a cross-linked polymer, and at least one mineral, wherein:

(i) said cross-linked polymer comprises at least one cross-linker and a polymeric backbone comprising a plurality of monomeric units; and

(ii) said cross-linked polymer is characterized by a cross-linking density in the range of from $2x10^{20}$ to $2x10^{25}$ units/l, by total weight of said polymer.

2. The composition of claim 1, wherein said mineral comprises a ceramic material.

3. The composition of claim 2, wherein said ceramic material is selected from the group consisting of: alumina, quartz, zirconia, titania, silica, magnesia, silicon carbide, silicon nitride, boron carbide, boron nitride, aluminum nitride, cordierite, sialon yttria, or any mixture thereof.

4. The composition of claim 1, wherein said mineral is selected from the group consisting of: clay, calcium carbonate, aluminum hydroxide, magnesium hydroxide, aluminum oxide, or any combination thereof.

5. The composition of any one of claims 1 to 4, wherein a concentration of said mineral is in the range of from 75% to 95%, by total weight of said composite.

6. The composition of any one of claims 1 to 5, wherein said mineral is in the form of one or more particles, wherein a median diameter of said one or more particles is in the range of from 0.001 to 8 mm.

7. The composition of any one of claims 1 to 6, wherein said plurality of monomeric units comprises at least one acrylic monomeric unit.

8. The composition of claim 7, wherein said at least one acrylic monomeric unit is selected from the group consisting of: methyl methacrylate, 2-ethylhexyl acrylate, 2–ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate,

isobornyl acrylate, isobornyl methacrylate, acrylic acid, methacrylic acid, and any derivative or combination thereof.

9. The composition of any one of claims 1 to 8, wherein at least 45%, by weight, of said monomeric units are derived from one or more materials selected from the group consisting of: methacrylate, ethyl acrylate, and a combination thereof.

10. The composition of any one of claims 1 to 9, wherein said cross-linker is selected from the group consisting of: triethylene glycol diacrylate, trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol tetraacrylate, dipentaerithritol hexaacrylate, dendritic acrylates, and methacrylates having at least two functional groups, and any derivative or combination thereof.

11. The composition of any one of claims 1 to 10, wherein said cross-linked polymer comprises from 5% to 30% acrylic polymer, by total weight of said composite.

12. The composition of any one of claims 1 to 11, wherein a concentration of said cross-linked polymer is in the range of from about 5% to 30%, by weight of said composite.

13. The composition of any one of claims 1 to 12, wherein said composite further comprises a toughener.

14. The composition of claim 13, wherein said toughener is in the form of a core-shell structure.

15. The composition of claim 13, wherein said toughener is selected from the group consisting of: polyurethanes mono acrylate, polyurethanes diacrylate, polyurethanes triacrylate, or any combination thereof.

16. The composition of any one of claims 13 to 15, wherein said toughener is in an amount ranging from 2% to 20%, by weight, of said cross-linked polymer.

17. The composition of any one of claims 1 to 16, wherein said composite comprises less than 0.2% of styrene monomer, by weight.

18. The composition of any one of claims 1 to 17, wherein said composite comprises less than 0.01% transition metals, by weight.

19. The composition of any one of claims 1 to 18, wherein said composite is characterized by glass-transition temperature (T_g) in the range of from 55 to 110 °C.

20. The composition of any one of claims 1 to 19, wherein said composite is characterized by flexural strength in the range of from 45 to 110 MPa.

21. The composition of any one of claims 1 to 20, wherein said composite is characterized by young modulus in the range of from 10,000 to 30,000 MPa.

22. The composition of any one of claims 1 to 21, wherein said composite is characterized by toughness (G_{1c}) of at least 30 J/m^2.

23. The composition of any one of claims 1 to 22, wherein said composite is characterized by heat distortion temperature (HDT) of at least 55 °C.

24. The composition of any one of claims 1 to 23, wherein said composite is characterized by whiteness index change (ΔWI) of less than 25%, following ultraviolet (UV) radiation exposure thereto for 50 to 200 hours.

25. The composition of any one of claims 1 to 24, wherein said composite further comprises a linker attached to the polymeric backbone, wherein said linker is configured to contact said mineral.

26. The composition of claim 25, wherein said linker is physically attached to said mineral.

27. The composition of claim 26, wherein said linker is covalently attached to said polymeric backbone.

28. The composition of any one of claims 25 to 27, wherein said linker is derived from acryloyl.

29. The composition of any one of claims 25 to 27, wherein said linker comprises alkoxysilane.

30. The composition of any one of claims 25 to 29, wherein said linker is in amount ranging from 0.02% to 0.3%, by weight, of said composite.

31. A method for obtaining a composition comprising a composite, said composite comprising a cross-linked polymer and at least one mineral, the method comprising the steps of:

a. mixing a plurality of monomers, at least one cross-linker, a peroxide initiator, and optionally at least one toughener or one or more polymer stabilizers, thereby obtaining a mixture of the cross-linked polymer;

b. adding a mineral to said mixture;

c. curing said mixture at a temperature above 90°C, thereby obtaining said composition.

32. The method of claim 31, wherein the curing step further comprises a step of adding a linker to said mixture.

33. The method of any one of claims 31 and 32, wherein said peroxide initiator is selected from the group consisting of: di-benzoyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, cyclohexanone peroxide, methylethyl peroxide, tert-butyl peroxyoctoate, tert-butyl peroxybenzoate, dicumyl peroxide, 1,1-bis(tert-butyl peroxy)3,3,5-trimethylcyclohexane, tert-butyl peroxymaleate, and any derivative or combination thereof.

34. The method of any one of claims 31 to 33, wherein said monomers comprise one or more acrylic monomers.

Intellectual Property Office

Application No: GB1718089.4 **Examiner:** Mr Martin Price

Claims searched: 1-34 **Date of search:** 25 April 2018

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-34	JP H0539414 A Nippon Oils and Fats - see WPI abstract number 1993-096872
X	1-34	GB 2151187 A Ricoh - see e.g. the claims and examples
X	1-34	EP 1674513 A1 Rehau - see e.g. claim 1, example 3 and WPI abstract number 2006-473615
X	1-34	CA 1083617 A Stauffer - see e.g. claims 1, 11, 18 and 23
X	1-34	US 2008/0182193 A1 Agur - see e.g. claim 1 and paragraph 0058
X	1-34	JP H02253953 A France Bed - see WPI abstract number 1990-351961 and EPODOC abstract
X	1-34	CN 103130963 A Jiangsu Sunrising - see WPI abstract number 2013-R31463 and EPODOC abstract

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Field of Search:

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

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

C04B; C08F; C08J

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

EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
C08J	0003/24	01/01/2006
C04B	0024/26	01/01/2006
C04B	0026/04	01/01/2006
C08F	0002/44	01/01/2006