COMPOSITIONS COMPRISING AN ACRYLIC POLYMER AND PROCESSES OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of priority from UK Patent Application no. GB1718089.4 filed on November 1, 2017. The content of the above document is incorporated by reference in its entirety as if fully set forth herein.

FIELD OF INVENTION

[002] This invention is directed, *inter alia*, to a composite comprising a crosslinked acrylic polymer, and an inorganic aggregate and/or mineral.

BACKGROUND OF THE INVENTION

[003] Engineered stones are widely used as building materials e.g., for kitchen countertops, indoor and outdoor floors, dressing tables, bathtubs, wash bowls, and interior articles. Artificial stone products are in great demand due to their ability to be manufactured in a wide variety of patterns and colors that cannot be found in nature, and to show superior physical and mechanical performance, when compared to natural stone.

[004] 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 of the bending strength and the toughness of the engineered stones. Another disadvantage is the polyester's poor light fastness in an outdoor environment.

SUMMARY

[005] This disclosure is directed, *inter alia*, to a composite comprising a crosslinked acrylic polymer, and an inorganic aggregate and/or mineral.

[006] The present inventors have surprisingly uncovered that composites having a specific percentage range of cross-linked acrylic polymer and an inorganic aggregate and/or mineral exhibit exceptional mechanical properties and stability to U.V. irradiation.

[007] According to some examples of the present disclosure there is provided a composition comprising a composite, the composite comprising a cross-linked acrylic polymer and at least one

an inorganic aggregate and/or mineral, wherein the cross-linked acrylic polymer is present at a concentration of 5 to 17%, by weight of the composite.

[007a] In one aspect, there is disclosed a composite comprising: (a) a cross-linked acrylic polymer and (b) an inorganic aggregate in amount of 5 to 17%, by weight of said composite.

[007b] In another aspect, there is disclosed a composition comprising the composite as described herein.

[008] In some examples, the inorganic aggregate and/or mineral is selected from the group comprising of: quartz, quartzite, clay, calcium carbonate, aluminum hydroxide, magnesium hydroxide, or any combination thereof.

[009] In some examples, the inorganic aggregate and/or mineral is present at a concentration of 82% to 95%, by total weight of the composite.

[010] In some examples, the composite exhibits a CIELAB color shift (ΔE) of less than 3 after 1000 hours exposure to irradiance of 65 W/m^2 according to ISO 4892-2.

[011] In some examples, the composite exhibits a CIELAB b coordinate difference (Δb) of less than 3 after 1000 hours exposure to irradiance of 65 W/m^2 according to ISO 4892-2.

[012] In some examples, 82% to 94%, by weight, of an inorganic aggregate and/or mineral is in the form of one or more particles having a median diameter in the range of 0.001 to 4 mm.

[013] In some examples, the acrylic polymer comprises a plurality of monomeric units selected from acrylate, or any derivative thereof.

[014] In some examples, the acrylate is selected from: methacrylate, methyl methacrylate (MMA), 2-ethylhexyl acrylate (2-EHA), 2–ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and any derivative or combination thereof. In some examples, the monomeric unit comprises 2-EHA and MMA. In some examples, the MMA and 2-EHA are present at a weight ratio ranging from 5:1 to 3:1, respectively.

[015] In some examples, the cross-linked acrylic polymer comprises a cross-linker selected from the group comprising of: triethylene glycol diacrylate, trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol tetraacrylate, dipentaerithritol hexaacrylate, dendritic acrylates, and methacrylates having at least two functional groups, or any derivative or combination thereof.

[016] In some examples, the composite further comprises a toughener. In some examples, the toughener is selected from the group comprising of: urethane mono acrylate, urethane diacrylate, urethane triacrylate, or any combination thereof. In some examples, the toughener is present at a concentration of 0.5% to 15%, by weight of the cross-linked polymer.

[017] In some examples, the composite is characterized by glass-transition temperature (T_g) in the range of from 50 to 90 °C.

[018] In some examples, the composite is characterized by flexural strength in the range of 45 to 95 MPa.

[019] In some examples, the composite is characterized by Young's modulus in the range of 11,000 to 25,000 MPa.

[020] In some examples, the composite is characterized by heat distortion temperature (HDT) of at least 55°C.

[021] In some examples, the composite further comprises a coupling agent attached to a backbone of the polymer, wherein the coupling agent is configured to contact the inorganic aggregate and/or mineral.

[022] In some examples, the coupling agent is physically attached to the inorganic aggregate and/or mineral. In some examples, the coupling agent is covalently attached to the polymeric backbone. In some examples, the coupling agent is derived from acryloyl. In some examples, the coupling agent comprises alkoxysilane. In some examples, the coupling agent is present at a concentration ranging from 0.02% to 0.4%, by weight of the composite.

[023] According to some examples of the present disclosure there is provided a method for obtaining a composition comprising a composite, the composite comprising a cross-linked acrylic polymer and at least one inorganic aggregate and/or mineral, the method comprising the steps of:

a. mixing a plurality of acrylic monomers, at least one cross-linker, a radical initiator, and optionally at least one agent selected from: a toughener, and polymer stabilizer, thereby obtaining a mixture of the cross-linked polymer;

b. adding an inorganic aggregate and/or mineral to the mixture, the inorganic aggregate and/or mineral being at a concentration of 80% to 95%, by weight of the mixture, and

c. curing the mixture at a temperature of above 80°C, thereby obtaining the composition.

[023a] In one aspect, there is provided a method for obtaining a composite comprising a cross-linked acrylic polymer and at least one inorganic aggregate, the method comprising the steps of:

a. mixing a plurality of acrylic monomers, at least one cross-linker, and a radical initiator, thereby obtaining a mixture of the cross-linked polymer;

b. adding an inorganic aggregate to said mixture, the inorganic aggregate and/or mineral being present at a concentration of 80% to 95%, by weight of said mixture, and

c. curing said mixture at a temperature of above 80 °C, thereby obtaining said composition.

[024] In some examples, the curing step further comprises a step of adding a radical initiator to the mixture.

[025] In some examples, the initiator is selected from the group comprising 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, Azobisisobutyronitrile (AIBN), and any derivative or combination thereof.

[026] 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 examples 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[027] Some embodiments of the invention are herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of embodiments of the invention. In this regard, the description taken with the drawings makes apparent to those skilled in the art how embodiments of the invention may be practiced.

[028] In the drawings:

[029] FIGs. 1A-1C present photographs demonstrating cracks/breaks in the slabs as described in Table 5 below: "Grain 1" (5% acrylic resin) after pressing (FIG. 1A) and after curing (FIG. 1B); and "Grain 6" (showing slab made of non-powder: powder fraction weight ratio of 12.2): demonstrating dry areas and crumbling after curing (FIG. 1C).

[030] FIG. 2 presents a photograph demonstrating cracks in the slab of "Fine 1" (11% acrylic resin) as described in Table 6 below, after pressing.

[031] FIGs. 3A-3C present photographs demonstrating the slab as described in Table 6 below: "Fine 4" (19.5% acrylic resin) upon pressing (FIG. 3A) and the bubbles formed in the slab after curing (FIG. 3B); and "Fine 7" showing slab made of non-powder: powder fraction weight ratio of 1.3: demonstrating many paper notches (impossible to polish) after curing (FIG. 3C).

DETAILED DESCRIPTION OF THE INVENTION

[032] The present invention, in some embodiments thereof, is directed to a composite comprising a cross linked polymeric backbone having acrylic monomeric units, and inorganic aggregate and/or mineral. In one embodiment, a mineral is in the form of an aggregate or a “mineral aggregate”. In one embodiment, a mineral or a mineral aggregate comprises/consists a single mineral type. In one embodiment, a mineral or a mineral aggregate comprises/consists a mixture of different mineral types.

[033] 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