

STRAIN HARDENING MAGNESIUM SILICATE HYDRATE COMPOSITES
(SHMSHC)

Cross-Reference to Related Application

5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10202012380V, filed 10 December 2020, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

10 [0002] The present disclosure relates to a strain hardening cement pre-mix and a strain hardening magnesium-silicate-hydrate composite. The present disclosure also relates to a method of forming the strain hardening cement pre-mix and a method of forming the strain hardening magnesium-silicate-hydrate composite.

15 **Background**

[0003] Strain hardening cementitious composites (SHCC) may be categorized as a group of construction materials with superior mechanical properties and environmental durability. SHCC may achieve at least 1% tensile strain capacity, which may be about a hundred times that of conventional concrete. The extraordinary tensile properties may be achieved by the addition of a small portion of fibers, which helps the formation of multiple microcracks with tight crack width instead of few large cracks seen in conventional concrete. The superior tensile ductility together with tight crack width induces stronger corrosion resistance and potential to engage self-healing of cracks in SHCC. While a wide range of fibers, such as metallic fibers, have been used to manufacture SHCC, the selection of matrix composition has been rather constrained with Portland cement being the hydraulic cement traditionally used.

20 [0004] Magnesium-silicate-hydrate (M-S-H, or just MSH) may have gained attention over the past years. Compared to hydraulic Portland cement, M-S-H matrix relies on hydration for strength development, therefore M-S-H composites do not require any special accelerated CO₂ curing conditions as opposed to MgO-based samples that rely on carbonation for strength development. M-S-H formation occurs in the presence of
30 MgO and silica sources with the aid of water in hydration reaction. The reaction

between the dissolved ions of MgO and silica sources leads to formation of a dense gel-like M-S-H structure, often resulting in significant levels of strengths. This system may be used in various applications due to its high compressive strength (e.g. 70 MPa at 28 days) and lower pH values (10-10.5 as compared to a pH of 13.5 for concrete formed using Portland cement) that are suitable for chemical waste encapsulation.

[0005] M-S-H cement may be considered over Portland cement in certain instances for the following reasons. First is the lower energy requirements and CO₂ emissions of the production of the raw materials (i.e. MgO and SiO₂). The mineral calcination temperature for the manufacturing of reactive MgO (about 750 °C) is much lower than that of Portland cement (about 1450°C), which enables the use of alternative fuels and silica tends to be available in the form of by-products. Second is that M-S-H cement may have low intrinsic pH that allows utilization of the M-S-H cement in waste encapsulation applications. This renders M-S-H a potential green cement to replace the conventional Portland cement. Despite these considerations, M-S-H cement has its limitations.

[0006] As one example, M-S-H tends to have intrinsically lower pH values as mentioned above when compared to concrete formed using Portland cement. The low pH values may render an environment unsuitable for fibers, such as metallic fibers (which are used in traditional SHCC) due to potential corrosion or degradation. Also, traditional M-S-H tends to be brittle and hence not suitable for reinforcement by such fibers (e.g. steel bars/fibers). Such limitations of traditional M-S-H in turn tend to render M-S-H unsuitable for use with SHCC and vice versa.

[0007] There is thus a need to provide for a solution that addresses one or more of the limitations mentioned above. The solution should at least provide for a strain hardening magnesium-silicate-hydrate composite that integrates SHCC and MSH to provide superior mechanical/durability performance and to address environmental sustainability concerns, wherein the strain hardening MSH composite may be a strain hardening brittle matrix composite.

Summary

[0008] In a first aspect, there is provided for a strain hardening cement pre-mix that includes:

a reactive magnesium oxide cement;
an amorphous silica source; and
a fiber.

[0009] In another aspect, there is provided a strain hardening magnesium-silicate-hydrate composite formable from the strain hardening cement pre-mix described in various embodiments of the first aspect, which includes:

magnesium-silicate-hydrate; and
a fiber dispersed therein.

[0010] In another aspect, there is provided a method of forming the strain hardening cement pre-mix described in various embodiments of the first aspect, the method includes:

mixing an amorphous silica source with a reactive magnesium oxide cement to form a dry mixture; and
dispersing a fiber in the dry mixture.

[0011] In another aspect, there is provided a method of forming the strain hardening magnesium-silicate-hydrate composite described in various embodiments herein, the method includes:

mixing a reactive magnesium oxide cement with water;
mixing an amorphous silica source to the reactive magnesium oxide cement and the water to form a mixture;
dispersing a fiber in the mixture; and
curing the mixture including the fiber to form the strain hardening magnesium-silicate-hydrate composite.

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Brief Description of the Drawings

[0012] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the present disclosure. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

10 [0013] FIG. 1A is a plot of uniaxial tensile stress-strain curves of SHMSHC prepared with 1.2% or 0.0% oil-coated PVA fibers.

[0014] FIG. 1B is a table indicating mechanical properties of SHMSHC with 1.2% and 0.0% oil coated PVA fibers.

[0015] FIG. 1C is a table indicating the number of cracks and crack spacing of SHMSHC with 1.2% and 0.0% oil coated PVA fibers.

5 [0016] FIG. 2A is a micrograph of M-S-H sample showing the formed multiple cracks. Scale bar denotes 0.1 mm. The rectangle denoted (b) is zoomed in for a magnified image of the crack shown in FIG. 2B.

[0017] FIG. 2B is a micrograph of M-S-H sample showing the zoomed in image of a crack of FIG. 2A. Scale bar denotes 10 μ m.

10 [0018] FIG. 3A is a table indicating the chemical composition of MgO, MS, PC and fly ash (as obtained from suppliers).

[0019] FIG. 3B is a table indicating properties of the PVA fibers (obtained from supplier company).

[0020] FIG. 3C is a table indicating mix compositions of the SHMSHC and SHCC M45
15 mixes.

[0021] FIG. 4 shows a single fiber pull-out test experimental setup.

[0022] FIG. 5 is a plot of a single fiber pull-out load-displacement curve.

[0023] FIG. 6 illustrates the fiber bridging constitutive law.

[0024] FIG. 7 is a plot of Tensile stress-strain curves of SHMSHC and SHCC M45.

20 [0025] FIG. 8 is a table indicating Mechanical properties of SHMSHC and SHCC M45.

[0026] FIG. 9A is an image showing morphology of fracture surfaces of SHMSHC specimen. Scale bar denotes 1 mm.

[0027] FIG. 9B is an image showing morphology of fracture surfaces of SHCC M45 specimen. Scale bar denotes 10 mm.

25 [0028] FIG. 10A is an image showing visual appeal of a cracked SHMSHC specimen after the uniaxial tensile tests. Scale bar denotes cm.

[0029] FIG. 10B is an image showing visual appeal of a cracked SHCC M45 specimen after the uniaxial tensile tests. Scale bar denotes cm.

[0030] FIG. 11A is a field emission scanning electron microscopy (FESEM) image of
30 multiple crack formation in the SHMSHC specimen. The rectangle denoted (b) is zoomed in for a magnified image of the crack shown in FIG. 11B.

[0031] FIG. 11B is a FESEM image of a microcrack in the SHMSHC specimen.

- [0032] FIG. 12 is a plot showing residual crack width distributions of SHMSHC and SHCC M45 specimens.
- [0033] FIG. 13 is a table indicating average residual crack width and average crack spacing of SHMSHC and SHCC M45.
- 5 [0034] FIG. 14 is a plot of the load-displacement curves of a single PVA fiber pulled out from the M-S-H (or PC-based M45) matrix.
- [0035] FIG. 15 is a table indicating fiber/matrix interface bond properties of SHMSHC and SHCC M45 obtained from single fiber pull-out tests. β_1 denotes initial slip hardening coefficient.
- 10 [0036] FIG. 16 shows a morphology of fiber groove in M-S-H system after the pull-out of a PVA fiber.
- [0037] FIG. 17 is a table indicating the matrix properties of SHMSHC and SHCC M45 obtained from nano-indentation and three point bending on notched specimens.
- [0038] FIG. 18 is a plot of the indentation modulus and indentation hardness of indents
15 on SHMSHC and SHCC M45.
- [0039] FIG. 19 is a table indicating micromechanical parameters of SHMSHC and SHCC M45.
- [0040] FIG. 20 is a table indicating comparison of PSH indices of SHMSHC and SHCC M45.
- 20 [0041] FIG. 21 is a plot of the fiber bridging curves of SHMSHC and SHCC M45.
- [0042] FIG. 22 shows the single fiber pull-out test specimen preparation.
- [0043] FIG. 23 is a plot of a single fiber pull-out load-displacement curve with PE fibers being pulled out from PC matrix.
- [0044] FIG. 24A is a plot of the tensile stress-strain curves for 3 samples of SHMSHC
25 at PE fiber dosages of 2% by volume.
- [0045] FIG. 24B is a plot of the tensile stress-strain curves for 3 samples of SHMSHC at PE fiber dosages of 1% by volume.
- [0046] FIG. 24C is a plot of the tensile stress-strain curves for 3 samples of SHMSHC at PE fiber dosages of 0.5% by volume.
- 30 [0047] FIG. 24D is a plot of the tensile stress-strain curves for 3 samples of SHMSHC at PE fiber dosages of 0.25% by volume.

[0048] FIG. 24E is a table indicating the mechanical properties of SHMSHC at different PE fiber dosages.

[0049] FIG. 25A shows the morphology of fracture surfaces of SHMSHC at fiber dosages of 2% by volume. Scale bar denotes 1 cm.

5 [0050] FIG. 25B shows the morphology of fracture surfaces of SHMSHC at fiber dosages of 1% by volume. Scale bar denotes 1 cm.

[0051] FIG. 25C shows the morphology of fracture surfaces of SHMSHC at fiber dosages of 0.5% by volume. Scale bar denotes 1 cm.

10 [0052] FIG. 25D shows the morphology of fracture surfaces of SHMSHC at fiber dosages of 0.25% by volume. Scale bar denotes 1 cm.

[0053] FIG. 26A shows visual appearance of cracked SHMSHC specimens at fiber dosages of 2% by volume after the uniaxial tensile tests. Scale bar denotes 1 cm.

[0054] FIG. 26B shows visual appearance of cracked SHMSHC specimens at fiber dosages of 1% by volume after the uniaxial tensile tests. Scale bar denotes 1 cm.

15 [0055] FIG. 26C shows visual appearance of cracked SHMSHC specimens at fiber dosages of 0.5% by volume after the uniaxial tensile tests. Scale bar denotes 1 cm.

[0056] FIG. 26D shows visual appearance of cracked SHMSHC specimens at fiber dosages of 0.25% by volume after the uniaxial tensile tests. Scale bar denotes 1 cm.

20 [0057] FIG. 26E is a table indicating average residual crack width and average crack spacing of SHMSHC at different fiber.

[0058] FIG. 27 is a representative load-displacement curve of a single PE fiber pulled out from the M-S-H matrix.

[0059] FIG. 28A is a FESEM image of fiber groove with indications of multiple nodes. Scale bar denotes 100 μm .

25 [0060] FIG. 28B is a FESEM image of fibers with formation of nodes/bumps in the SHMSHC specimen. Scale bar denotes 100 μm .

[0061] FIG. 29 is a plot showing the relationship between fiber volume (V_f) and interface frictional force (τ_0).

30 [0062] FIG. 30 is a table that summarizes J_b' , J_{tip} , σ_0 , and σ_c values and corresponding PSH indices of SHMSHC. The table also compares PSH indices of SHMSHC at different fiber dosages.

[0063] FIG. 31 is a plot of the crack spacing at different PE fiber volumes (obtained from micromechanical model).

[0064] FIG. 32 is a table indicating various mix configurations of different binder, PE fiber and sand.

5 [0065] FIG. 33 shows materials used in mix designs sodium hexametaphosphate flakes (top left), magnesium oxide (MgO) (top center), micro silica (MS) (top right), silica sand (bottom left), river sand (bottom center), and polyethylene fibers (bottom right).

[0066] FIG. 34 shows a Hobart mixer (left image) and samples covered with plastic sheet (right image).

10 [0067] FIG. 35 shows a flow table before removing cone (top left image), after removing cone (top right image), and flow spread of the mix after 25 drops (bottom image).

[0068] FIG. 36 shows an IsoMet 4000 tool (left image) and enlarged section of a dog-boned specimen (right image).

15 [0069] FIG. 37 is a table indicating the mechanical properties of MSH samples with silica sand.

[0070] FIG. 38 is a table indicating the mechanical properties of MSH samples with river sand.

20 [0071] FIG. 39 shows tensile stress-strain plots of MSH-SS specimens (3 samples for each specimen), specifically MSH-00 (top image), MSH-SS-X (2nd row left image), MSH-SS-2X (2nd row right image), MSH-SS-3X (3rd row left image), and MSH-SS-4X (3rd row right image).

25 [0072] FIG. 40 shows tensile stress-strain plots of MSH-RS specimens (3 samples for each specimen), specifically MSH-00 (top image), MSH-RS-X (2nd row left image), MSH-RS-2X (2nd row right image), MSH-RS-3X (3rd row left image), and MSH-RS-4X (3rd row right image).

[0073] FIG. 41 is a table showing crack properties of MSH samples with silica sand.

[0074] FIG. 42 is a table showing crack properties of MSH samples with river sand.

30 [0075] FIG. 43 is a plot showing relationship between ultimate tensile strength and sand/binder ratio.

[0076] FIG. 44 is a plot showing relationship between tensile strain capacity and sand/binder ratio.

[0077] FIG. 45 shows fiber pull-out of MSH-SS (left image) and MSH-RS (right image) specimens.

[0078] FIG. 46 shows crack patterns of MSH-00 (top image), MSH-SS-X (2nd row left image), MSH-SS-2X (2nd row right image), MSH-SS-3X (3rd row left image), and
5 MSH-SS-4X (3rd row right image).

[0079] FIG. 47 shows crack patterns of MSH-00 (top image), MSH-RS-X (2nd row left image), MSH-RS-2X (2nd row right image), MSH-RS-3X (3rd row left image), and MSH-RS-4X (3rd row right image).

[0080] FIG. 48 is a plot of the relationship between average crack width and
10 sand/binder ratio.

[0081] FIG. 49 is a plot of the relationship between average crack spacing and sand/binder ratio.

Detailed Description

15 [0082] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the present disclosure may be practised.

[0083] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments.

20 Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

25 [0084] The present disclosure relates to a strain hardening cement pre-mix. When the pre-mix is mixed with water, it can form a strain hardening magnesium-silicate-hydrate (MSH) composite. As the pre-mix with water is an aqueous suspension for forming the MSH composite, the pre-mix may be termed herein “a cementitious composition”. The strain hardening magnesium-silicate-hydrate (MSH) composite of the present
30 disclosure may be abbreviated “SHMSHC” and exchangeably termed herein “cured cementitious composition”, or “composite” for brevity.

[0085] Details of various embodiments of the present pre-mix and strain hardening magnesium-silicate-hydrate composite, and advantages associated with the various embodiments are now described below. Where the embodiments and/or advantages have been described in the example section further hereinbelow, they shall not be reiterated for brevity.

[0086] In the present disclosure, there is provided a strain hardening cement pre-mix that includes a reactive magnesium oxide cement, an amorphous silica source, and a fiber. As mentioned above, the pre-mix can be used to form a strain hardening magnesium-silicate-hydrate composite by mixing the pre-mix with water. That is to say, the pre-mix is formed of dry components. These dry components, when mixed with water, forms an aqueous suspension in which hydration may occur for forming the strain hardening magnesium-silicate-hydrate composite (also referred to as “a cured cementitious composition”). However, in the absence of water, the various components can be mixed together to form a dry solid mixture, i.e. the pre-mix of the present disclosure. In the context of the present disclosure, the reactive magnesium oxide cement and the amorphous silica source may be collectively referred to as “binder” in the pre-mix.

[0087] In various embodiments, the amorphous silica source may include microsilica, rice husk ash, or waste glass. The amorphous silica source contributes to the formation of magnesium-silicate-hydrate in the strain hardening magnesium-silicate-hydrate composition of the present disclosure.

[0088] In various embodiments, the fiber may include a polymeric fiber, a metallic fiber, or a naturally-occurring fiber. The fiber may be one or more of any suitable discontinuous fibers and may be provided in a bundled form of fibers. Non-limiting examples of the fiber may include polyvinyl alcohol (PVA) fiber, ethyl vinyl acetate (EVOH) fiber, polyethylene (PE) fiber, acrylic fibers, polypropylene (PP) fiber, acrylamide fiber, and natural fibers (e.g. sisal, eucalyptus, pine, jute fiber).

[0089] In various embodiments, the fiber may be present in an amount of 15 vol% or less, 10 vol% or less, 5 vol% or less, etc. Other non-limiting examples of the amount of fiber present are described in the example section hereinbelow.

[0090] In certain non-limiting embodiments, the fiber may be coated with an oiling agent or carbon nanofiber.

[0091] In various embodiments, the fiber may have a diameter ranging from 10 μm to 100 μm , 20 μm to 100 μm , 30 μm to 100 μm , 40 μm to 100 μm , 50 μm to 100 μm , 60 μm to 100 μm , 70 μm to 100 μm , 80 μm to 100 μm , 90 μm to 100 μm , etc. In various embodiments, the fiber may have a length ranging from 5 mm to 30 mm, 10 mm to 30 mm, 15 mm to 30 mm, 20 mm to 30 mm, 25 mm to 30 mm, etc. Other non-limiting examples of the diameter and length of the fiber are described in the example section hereinbelow.

[0092] In various embodiments, the reactive magnesium oxide cement may be present in an amount of 30 wt% to 70 wt%, 40 wt% to 70 wt%, 50 wt% to 70 wt%, 60 wt% to 70 wt%, etc., based on the reactive magnesium oxide cement and the amorphous silica source, and/or the amorphous silica source may be present in an amount of 30 wt% to 70 wt%, 40 wt% to 70 wt%, 50 wt% to 70 wt%, 60 wt% to 70 wt%, etc., based on the reactive magnesium oxide cement and the amorphous silica source.

[0093] In various embodiments, the strain hardening cement pre-mix may further include a water reducing agent, a viscosity controlling agent, and/or an aggregate. These components may be present in solid powder form in the pre-mix. Non-limiting examples of water reducing agent may include sodium hexametaphosphate (NaHMP, i.e. $\text{Na}(\text{PO}_3)_6$), sodium trimetaphosphate, sodium orthophosphate, and Sika ViscoCrete-5-555. Non-limiting examples of viscosity controlling agent may include cellulose ethers, starch, and natural gum. Non-limiting examples of the aggregate may include micro silica sand, river sand, basalt, granite, limestone, sandstone, marble, and quartz.

[0094] As mentioned above, the present disclosure also relates to a strain hardening magnesium-silicate-hydrate composite formable from the strain hardening cement pre-mix described in various embodiments hereinabove. The strain hardening magnesium-silicate-hydrate composite may include magnesium-silicate-hydrate, and a fiber dispersed therein. Embodiments and advantages described for the present pre-mix of the first aspect can be analogously valid for the present strain hardening magnesium-silicate-hydrate composite subsequently described herein, and vice versa. As the various embodiments and advantages have already been described above and in the examples demonstrated herein, they shall not be iterated for brevity.

[0095] In various embodiments, the fiber may include a polymeric fiber, a metallic fiber, or a naturally-occurring fiber. Other embodiments of the fiber have already been described above.

5 [0096] In various embodiments, the fiber may be present in an amount of 15 vol% or less, 10 vol% or less, 5 vol% or less, etc. In certain non-limiting embodiments, the fiber may be coated with an oiling agent or carbon nanofiber.

[0097] In various embodiments, the fiber may have a diameter ranging from 10 μm to 100 μm . In various embodiments, the fiber may have a length ranging from 5 mm to 30 mm. Other embodiments concerning diameter and length of the fiber have already been
10 described above.

[0098] In various embodiments, the strain hardening magnesium-silicate-hydrate composite may further include a water reducing agent, a viscosity controlling agent, and/or an aggregate. Non-limiting examples of the water reducing agent, viscosity controlling agent, and aggregate have been described above and in the examples section
15 further hereinbelow.

[0099] The present disclosure also relates to a method of forming the strain hardening cement pre-mix. Embodiments and advantages described for the present pre-mix of the first aspect can be analogously valid for the present method subsequently described herein, and vice versa. As the various embodiments and advantages have already been
20 described above and in the examples demonstrated herein, they shall not be iterated for brevity.

[00100] The method may include mixing an amorphous silica source with a reactive magnesium oxide cement to form a dry mixture, and dispersing a fiber in the dry mixture.

[00101] In various embodiments, the method may further include mixing the dry mixture with a water reducing agent, a viscosity controlling agent, and/or an aggregate.

[00102] The present method of forming the strain hardening cement pre-mix is
25 described in more detail in the example section further hereinbelow.

[00103] The present disclosure further relates to a method of forming the strain hardening magnesium-silicate-hydrate composite. Embodiments and advantages described for the present pre-mix of the first aspect and the strain hardening magnesium-silicate-hydrate composite can be analogously valid for the present method

subsequently described herein, and vice versa. As the various embodiments and advantages have already been described above and in the examples demonstrated herein, they shall not be iterated for brevity.

[00104] The method may include mixing a reactive magnesium oxide cement with
5 water, mixing an amorphous silica source to the reactive magnesium oxide cement and the water to form a mixture, dispersing a fiber in the mixture, and curing the mixture comprising the fiber to form the strain hardening magnesium-silicate-hydrate composite.

[00105] In various embodiments, the method may further include mixing the water
10 with a water reducing agent and/or a viscosity controlling agent prior to mixing the reactive magnesium oxide cement with the water.

[00106] In various embodiments, curing the mixture may include curing the mixture for at least 28 days at a relative humidity of at least 60% and at a temperature more than 0°C and less than 60°C. The present method of forming the strain hardening
15 magnesium-silicate-hydrate composite is described in more detail in the example section further hereinbelow.

[00107] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the present disclosure.

[00108] In the context of various embodiments, the articles “a”, “an” and “the” as used
20 with regard to a feature or element include a reference to one or more of the features or elements.

[00109] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[00110] As used herein, the term “and/or” includes any and all combinations of one or
25 more of the associated listed items.

[00111] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited
30 elements.

Examples

[00112] The present disclosure relates to a strain hardening M-S-H composite (SHMSHC) reinforced with short and randomly oriented PVA microfibers demonstrated in various examples herein. Mechanical properties were tested and damage patterns in terms of crack width and crack spacing were characterized. Single fiber pull-out tests were performed to assess the interface bond properties between the PVA fiber and the M-S-H matrix. Matrix properties (i.e. indentation modulus and hardness, and fracture toughness) were evaluated by means of nano-indentation and three point bending tests. Micromechanics-based models were used to calculate the fiber bridging behavior and to assess the strain hardening potential of the resulting SHMSHC. All results were compared with and benchmarked against the most studied PC-based PVA-SHCC M45 system.

[00113] Regarding magnesium-silicate-hydrate (M-S-H) cement, it may serve as an alternative cement with potentially lower energy requirements and emissions. Due to the intrinsically low pH values of its matrix, however, normal steel reinforcement is not appropriate for M-S-H system. To toughen the matrix and to overcome the brittle nature of the material, a strain hardening magnesium-silicate-hydrate composite (SHMSHC) is demonstrated herein by incorporating, as a non-limiting example, 2 vol.% short and randomly oriented polyvinyl alcohol (PVA) microfibers. The resulting SHMSHC exhibits significant strain hardening with a tensile strain capacity of more than 3%, a compressive strength beyond 50 MPa and a tensile strength of around 3 MPa. Remarkably, saturated multiple cracking with a tight crack width less than 10 μm invisible to the human naked eyes was observed. The SHMSHC developed herein addresses the challenges of M-S-H and helps widen possible application areas of M-S-H system.

[00114] As mentioned above, magnesium-silicate-hydrate (M-S-H) cement has attracted significant attention in the recent years as an alternative cement with potentially lower energy requirements and emissions. To improve the naturally brittle tensile behavior of the M-S-H cement, a strain hardening magnesium-silicate-hydrate composite (SHMSHC) is presently developed by incorporating, as another non-limiting example, short and randomly oriented polyethylene (PE) microfibers in several dosages. The resulting SHMSHC exhibits significant strain hardening with a tensile

strain capacity of more than 7% at reduced fiber dosages such as 1 and 0.5 vol%. Saturated multiple cracking with a narrow crack spacing around 0.9 mm was observed even at uncommonly low fiber content (i.e. 0.5 vol%). The developed SHMSHC presents a cost-effective solution to the fundamental economical challenge of fiber reinforced composites. The SHMSHC with PE fibers has the potential to be utilized in a range of applications due to its high ductility (beyond 7%) and potentially lower costs due to reduced fiber dosages.

[00115] The present strain hardening magnesium-silicate-hydrate composite, a pre-mix for forming the present strain hardening magnesium-silicate-hydrate composite, and their respective methods of forming, are described in further details, by way of non-limiting examples, as set forth below.

[00116] Example 1A: Overview of strain hardening magnesium-silicate-hydrate composite

[00117] Traditional fiber reinforced strain hardening cementitious composites (SHCC), as a type of high performance construction material, may require a high Portland cement content. The production of Portland cement consumes high amounts of energy and results in the emissions of a high amount of CO₂. It is therefore of interest to replace Portland cement with a more sustainable alternative in the preparation of SHCC. Magnesium silicate hydrate, also termed herein as “magnesium-silicate-hydrate (M-S-H) matrix”, on the other hand, is brittle and tends to have difficulty being reinforced with traditional steel reinforcing bar due to the high risk of rebar corrosion. It may therefore be highly desirable to enhance the toughness of such material which can greatly widen the potential applications of magnesium silicate hydrate (M-S-H) cement. In the present disclosure, a strain hardening brittle matrix composite (also termed herein as “strain hardening magnesium-silicate-hydrate composite”) obtained through the use of magnesium silicate hydrate is described. The workability of the M-S-H matrix combined with uniformly distributed short fibers is demonstrated in various examples herein.

[00118] SHCC may be a superior construction material but not environment-friendly due to the high Portland cement usage. Magnesium silicate hydrate (M-S-H) presents sustainability advantages due to lower manufacturing temperatures of MgO and availability of silica sources even in the form of waste materials. The present disclosure

integrates M-S-H into SHCC, resulting in a sustainable construction material. Compared with traditional Portland cement-based SHCC, the new composition can reduce the CO₂ emissions, from raw material manufacturing to SHCC field application, by at least 40-60%.

5 [00119] M-S-H concrete is brittle and tends to be difficult for reinforcing with traditional steel reinforcing bar. This is because carbonation of M-S-H reduces pH of matrix which causes depassivation of steel reinforcement and subsequent corrosion. That said, with exceptional mechanical properties such as high tensile ductility, high damage tolerance, and fine crack width, such resulting strain hardening M-S-H
10 composites (SHMSHC) may be used in applications where reinforcement is not necessary such as retrofitting of unreinforced masonry walls, pavement overlays, and surface repair of dams and earth retaining walls. Other potential applications of unreinforced SHMSHC include shotcrete for underground rock cavern and tunnel linings.

15 [00120] To address the shortcomings mentioned above, the present disclosure provides for a cementitious composition (i.e. the pre-mix) and a method of forming the same. The cementitious composition may be used for forming strain hardening magnesium silicate hydrate composite.

[00121] The cementitious composition may be an aqueous suspension when mixed
20 with water, wherein the aqueous suspension may include magnesium oxide cement (e.g. reactive magnesium oxide cement (RMC)) and an amorphous silica source (e.g. microsilica), and one or more fibers dispersed therein. Prior to forming the aqueous suspension, a pre-mix (i.e. the cementitious composition) may be first prepared. This pre-mix may include the reactive magnesium oxide cement, the amorphous silica
25 source, and the one or more fibers. This pre-mix may be termed herein “strain hardening cement pre-mix”. The pre-mix may be mixed with water to form the aqueous suspension. In certain non-limiting instances, as an alternative, a method of forming the aqueous suspension may include forming a suspension from a binder comprising magnesium oxide cement and microsilica, and dispersing one or more fibers to the
30 suspension to form a mixture.

[00122] The aqueous suspension comprising the cementitious composition may be cured at a relative humidity of 50% or more, 60% or more, etc., to form a magnesium

silicate hydrate composite including the one or more fibers. Such a magnesium silicate hydrate composite may be exchangeably termed herein “strain hardening magnesium-silicate-hydrate composite (SHMSHC)” and “cured cementitious composition”. The CO₂ level of the curing environment can be ambient, i.e. this composition based on the formation of M-S-H does not require special CO₂ curing arrangements. However, accelerated CO₂ curing conditions does not compromise the process either. The curing temperature does not require adjustments either from ambient conditions. However, extremely high (e.g. >60 °C) or extremely low temperatures (e.g. < 0 °C) should be avoided as it may affect the availability of the water in the pore solution for hydration reaction. It should be noted that the hydration reaction proceeds as long as the internal humidity of the cementitious composition is above 85%. Accordingly, the cured cementitious composition may include a magnesium silicate hydrate composition containing the one or more fibers.

[00123] The cementitious composition may further include a water reducing agent, a viscosity controlling agent, one or more supplementary binders and/or one or more fine or coarse aggregates. In this regard, the method of forming a cementitious composition may be modified, that is, the one or more fibers may be surface modified to tune the interfacial bond between the one or more fibers and the binder. For example, an oiling agent may be coated on the one or more fibers or the surface of one or more fibers may be coated with carbon nanofibers (CNFs).

[00124] Example 1B: General discussion of strain hardening magnesium-silicate-hydrate composite and a pre-mix

[00125] Demonstration of the present examples involves using fibers to reinforce brittle matrix containing reactive MgO and microsilica as the binder. The resulting strain hardening magnesium silicate hydrate composites (SHMSHC) can have a density ranging from 1,000 to 2,500 kg/m³, and a tensile ductility of at least 1%, e.g., from 1% to 20%. The tensile strain capacity of SHMSHC may depend on the type of fiber, matrix properties and interface properties between fiber/matrix. Depending on the matrix design and selection of the fibers, SHMSHC often exhibit strain capacities much beyond 1%, e.g., from 1% to 20%.

[00126] The mixture of SHMSHC can include MgO cement, microsilica, water, and fiber in different proportions. Other optional constituents, such as water reducing agents

and viscosity controlling agents, may be needed to adjust thixotropic rheology and viscosity characteristics to achieve adequate workability and disperse the fibers uniformly. Phosphate based chemicals such as sodium hexametaphosphate, trimetaphosphate and/or orthophosphate, which can be used as water reducing agents
5 (while they may also affect the viscosity of the mix), may be included in the mix to avoid high water contents. These agents may be included (but not limited to) around 1-4% of the total binder mass (i.e., based on MgO cement and microsilica only). In some mixes, viscosity controlling agents including cellulose ethers, starch and/or natural gums may be used from 0.1 to 2 wt.% of the total binder mass. Fine or coarse aggregates
10 can also be added to alter the toughness of the matrix and to introduce imperfections to initiate crack formation. For example, crystalline silica may be added as fine aggregates. [00127] Reactive MgO cement used in the present disclosure is obtained from the calcination of magnesium carbonate or magnesium hydroxide at temperatures lower than 1000°C. Amorphous SiO₂, e.g., microsilica, that is used in the examples is
15 commercially available, however it can be obtained as a waste product as well. Other amorphous silica sources including but not limited to rice husk ash (RHA) and waste glass (WG) can also be used as silica source. Other supplementary binders, like hydraulic cement, coal fly ash, and ground granulated blastfurnace slag may be added as optional supplements. The addition of such supplementary binders from industrial
20 wastes can greatly reduce the cost of the composite and contribute to mechanical performance through cementitious and pozzolanic reactions. The fraction of reactive MgO cement in binder may range from 30% to 70% by mass of the binder (based on MgO cement and microsilica only). The microsilica content may vary from 30 to 70% of the total binder mass. It may be preferred that the size of microsilica is compatible
25 with the size of MgO cement. For example, majority of the MgO and microsilica particles may have a particle size of smaller than 150 µm. The binders set in the presence of water and gain strength via hydration reaction over time. [00128] Water may be present in the fresh mixture, optionally in conjunction with a water reducing agent to achieve adequate rheological properties. A water-to-binder (i.e.,
30 MgO and microsilica only) ratio ranging from 0.3 to 0.8 can be used to achieve the desired strength. The water reducing agent is used to adjust the desired workability level after the water content in the composite is determined. The quantity of water reducing

agent needed varies with the water-to-binder ratio, composition of binder, and type of water reducing agent. A non-limiting example of a water reducing agent may include sodium hexametaphosphate (NaHMP) ($\text{Na}(\text{PO}_3)_6$) solution. Other water reducing agents can include sodium trimetaphosphate or sodium orthophosphate or Sika ViscoCrete-5-555 or any suitable water reducing agent. The amount of water reducing agent can be from about 1% to 4% of the binder (i.e., MgO cement and microsilica only) by mass.

[00129] The fibers may be one or more of any suitable discontinuous fibers and are preferably provided in a bundled form. Examples of suitable fibers include but are not limited to metallic fibers, polymeric fibers (e.g. polyvinyl alcohol (PVA) fibers, ethyl vinyl acetate (EVOH) fibers, polyethylene (PE) fibers, acrylic fibers, polypropylene (PP) fibers, acrylamide fibers) and natural fibers (e.g. sisal, eucalyptus, pine fibers).

[00130] The amount of fibers in the mixture may vary with the design of the mix they are included in as well as the nature and size of the fibers. The amount should be sufficient for the provision of necessary ductility (tensile strain capacity of about 1% to 20%, and more preferably of about 3% to 7%) to the composition at the low end of the included concentration, and a sufficiently low amount on the high end to allow self-compaction. More fibers may provide more bridging strength however it may compromise the rheology of the mix. Therefore, it is a balance and it requires a careful configuration of the mix. In general, with conventional fiber sizes, compaction may be difficult without vibration if the fiber content exceeds 2.5%. Fibers are preferably included in SHMSHC at a range of 0.5 to 10% by volume, more preferably at an amount of about 1% to 3% by volume, and most preferably 1% to 2% by volume. The vol% is calculated based on the total fresh volume of the batch (i.e. total volume of all materials immediately after mixing). This includes the binder (i.e. MgO, microsilica), water, water reducing agent (if any), viscosity controlling agent (if any), supplementary binder (if any), fine and/or coarse aggregates (if any) and fibers.

[00131] The fibers preferably have a diameter of about 10-100 μm , more preferably of about 25-50 μm , and most preferably of about 35-45 μm , and a length of about 5-30 mm, more preferably of about 6-25 mm, and most preferably of about 6-18 mm.

[00132] Preferably, the fibers are hydrophilic fibers. In certain non-limiting preferred embodiments, hydrophilic PVA fibers are used. The surface of PVA fibers may be

coated with oiling agent (such as poly-oxymethylene, paraffin, Vaseline or any other suitable oil) by up to 1.5% by the weight of the fiber. The fibers may be coated with the oiling agent by any suitable manner, such as by dip-coating or spraying the hydrophilic fibers. Other oiling agents may be used as well. The hydrophilicity of PVA advantageously introduces strong interfacial bond between the fiber and surrounding matrix. The oiling agent is applied to prevent over-enhancement of the interfacial bond. Alternatively, the surface of one or more fibers may be coated with carbon nanofibers (CNFs), e.g. from 0.1 wt.% to 5 wt.%.

[00133] The nominal tensile strength of the fibers can vary from 500 to 3500 MPa.

Strong fibers can lead to stronger bridging strength and for most of the previously utilized strain-hardening composites fiber strengths around 1600 MPa are required. In the present examples, even relatively weaker (and therefore lower cost) fibers with around 550 MPa resulted in significant levels of ductility.

[00134] The fiber-reinforced cured cementitious compositions of the present disclosure may be prepared in the manner demonstrated herein. For example, the process for preparing fiber-reinforced cured cementitious composition may include the steps of (1) preparation of a water reducing agent and/or viscosity controlling agent (if present), for example $\text{Na}(\text{PO}_3)_6$ solution by dissolving the $\text{Na}(\text{PO}_3)_6$ flakes in predetermined amount of water, (2) mixing of the MgO powder with $\text{Na}(\text{PO}_3)_6$ solution for several minutes, (3) blending of microsilica powder into the mixture while mixing, (4) adding of any other supplementary binders such as fly ash, ground granulated blastfurnace slag and mixing until a homogenous paste is obtained, (5) if mortars are wanted, adding fine aggregates into the paste and mixing until the aggregates are homogeneously mixed with the paste, (6) adding fibers, such as hydrophilic PVA fibers into the fresh mixture and mixing until a homogenous mixture is achieved, and (7) curing in ambient air, optionally with accelerated CO_2 conditioning and/or optionally in a manually controlled environment until it achieves desirable mechanical strength. Curing may be carried out at a relative humidity of 60% or more and at any suitable temperatures. For example, curing may be carried out at temperature of from 15 °C to 60 °C .

[00135] **Example 1C: General discussion on examples of strain hardening magnesium-silicate-hydrate composite**

[00136] A non-limiting exemplary mix is demonstrated here for preparing the strain hardening magnesium silicate hydrate composites (SHMSHC). This mix includes reactive MgO, microsilica, water, $\text{Na}(\text{PO}_3)_6$, and fibers. The mix proportions are tabulated in Table 1. Reactive MgO provided by RBH Ltd. of United Kingdom, 5 microsilica provided by Elkem of Norway, and $\text{Na}(\text{PO}_3)_6$ provided by VMR Pte Ltd. of Singapore, were used in the mix. Reactive MgO and microsilica were used as the main binders, while the $\text{Na}(\text{PO}_3)_6$ was used as a water reducer to achieve the required workability for good fiber dispersion. The polyvinyl alcohol (PVA) fibers were manufactured by Kuraray Co. Ltd., Japan. The fiber length was 12 mm and the fiber 10 diameter was 39 μm . The fiber surface oil-coating content was 0.0% or 1.2%.

[00137] Table 1- mix proportions

Mix	PVA fiber type	Binder (wt. %)		Water/ Binder	$\text{Na}(\text{PO}_3)_6$ (by wt.% of total binder)	PVA fiber content (vol. %)
		MgO	Microsilica			
SHMSHC	0.0% or 1.2% oil- coating	50	50	0.40	2%	2.0

[00138] The mixture is prepared in a mixer with a planetary rotating blade. The mixing process followed these steps: 1) $\text{Na}(\text{PO}_3)_6$ was dissolved into the water, forming a 15 $\text{Na}(\text{PO}_3)_6$ solution; 2) reactive MgO powder was added into the $\text{Na}(\text{PO}_3)_6$ solution and mixed for two minutes in the planetary mixer; 3) microsilica powder was slowly added into the mixture while mixing; 4) this blend was mixed for over three minutes until a uniform paste without clumps was obtained; 5) PVA fibers were added into the mixture; 6) the mixing process continued for another three minutes.

20 [00139] The prepared fresh mixture was cast into dog bone-shaped molds for uniaxial tensile test. The specimens were removed from the molds after 1 day of preparation. Then they were cured in a sealed container (temperature = 30 °C, relative humidity = 90%) for twenty-eight days. Once curing was completed uniaxial tensile test was conducted with the dog-bone specimens at a loading rate of 0.5 mm/min.

25 [00140] FIG. 1A and 1B show the tensile stress-strain curves and mechanical properties of SHMSHC prepared using 1.2% or 0.0% surface oil-coated PVA fibers, respectively. The composites with 0.0% oil coated PVA fibers consistently exhibited strain capacities higher than 4.5%, while the ultimate tensile stress capacity reached over 2.50 MPa.

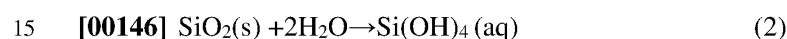
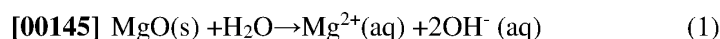
Meanwhile, when 1.2% oil coated PVA fibers were utilized, the composites reached comparatively lower strain capacities (~3.1%) as well as slightly lower ultimate tensile strengths (i.e. 2.3 MPa). The strain-hardening behaviour was obtained due to the formation multiple cracks for mixes with both type of PVA fibers (0.0% and 1.2% oil coated), however the number of cracks in the composites varied with the fiber type. The average number of cracks in the composites with 0.0% oil coated PVA fibers was ~58% higher in comparison to the composites with 1.2% oil coated PVA fibers (e.g. 153 vs 97), as can be seen in FIG. 1C. The higher number of cracks lead to a higher strain capacity and was indicative of a better crack saturation. This was reflected on the average crack spacing of the composites. The average crack spacing of composites with 0.0% oil coated PVA fibers was 0.9 mm, while this value was 1.3 mm for the composites with 1.2% oil coated PVA fibers. The differences in the mechanical performance and formation of cracks taking place only due to a change in the oil coating content of the fibers highlights the importance of the tailoring of mix design. It should be noted that reducing the oil content of the PVA fibers does not necessarily result in a better performance with every cement matrix. Contrary to what is observed in M-S-H matrix, a significantly better performance was demonstrated when 1.2% oil coated PVA fibers were used in PC matrix as opposed to 0.0% oil coated PVA fibers. The reason for this behaviour lies in the bond characteristics between the fiber and the cement matrix as well as the matrix properties such as matrix cracking toughness and elastic modulus. Therefore, in order to develop strain hardening composites with enhanced performances, efforts have to be made to understand fiber/matrix interface bond properties and the micromechanics behind the observed behaviours in the composites.

[00141] The micrographs presented in FIG 2A and 2B show formation of multiple cracks in a narrow area with tight crack spacing (FIG. 2A) and also a typical crack with a crack width of ~9.5 μm (FIG. 2B). Formation of multiple cracks with narrow spacings indicates the high crack saturation potential of SHMSHC, while the tight crack widths are beneficial for applications in terms low penetrability and potential of autogenous healing.

[00142] **Example 2A: Overview of strain hardening magnesium-silicate-hydrate composites (SHMSHC) reinforced with short and randomly oriented polyvinyl alcohol microfibers**

[00143] Portland cement (PC) production is responsible for around 8% of global annual anthropogenic carbon dioxide (CO₂) emissions. The increasing demand for PC production, coupled with the associated high energy requirements and significant contribution to greenhouse gas emissions, has created the need for an alternative cement. Reactive MgO-based binders, which may be synthesized from waste resources such as reject brine obtained from desalination plants may have emerged as an alternative with potentially lower energy requirements and emissions.

[00144] Magnesium-silicate-hydrate (M-S-H) cement, unlike carbonated MgO systems which rely on carbonation for strength gain, has a matrix that may gain strength via hydration, thereby not requiring any special elevated CO₂ curing environment. M-S-H formation occurs in the presence of MgO and silica sources, whose hydration determines the overall strength development. MgO and SiO₂ powders dissolve in water as shown in equations (1) and (2), respectively.



[00147] Accordingly, the reaction between the dissolved ions of MgO and silica sources leads to formation of a dense gel-like M-S-H structure, which results in high levels of strength. The chemical formula of the formed M-S-H gel tends to be not fixed and depends on several parameters involving the properties of raw materials, initial Mg/Si ratio, water content, and SHMP content. This system has the potential to be used in various applications due to its high compressive strengths (e.g. 70 MPa at 28 days) and low pH values that may be suitable for chemical waste encapsulation.

[00148] Strain hardening cementitious composites (SHCCs) may be a group of high performance fiber-reinforced cementitious composites that exhibit exceptional tensile ductility and multiple cracking behavior. The tensile ductility of SHCC may be several hundred times that of traditional concrete. The behavior of SHCC may be influenced by the matrix, fiber, and fiber/matrix interface properties. The design of SHCC may be guided by micromechanics-based principles. SHCC reinforced with polyvinyl alcohol (PVA) fibers exhibit high levels of strain capacities, while the crack width is self-controlled, typically with an average crack width of 40-80 μm.

[00149] Due to the intrinsically low pH values of its matrix, normal steel reinforcement is not appropriate for M-S-H system. Incorporation of non-metallic fibers could be a

feasible option to overcome the brittle nature of the material and to widen possible application areas of M-S-H system. In the present example, a strain hardening M-S-H composite (SHMSHC) reinforced with short and randomly oriented PVA microfibers was demonstrated. Mechanical properties were tested and damage patterns in terms of crack width and crack spacing were characterized. Single fiber pull-out tests were performed to assess the interface bond properties between the PVA fiber and the M-S-H matrix. Matrix properties (i.e. indentation modulus and hardness, and fracture toughness) were evaluated by means of nano-indentation and three point bending tests. Micromechanics-based models were used to calculate the fiber bridging behavior and to assess the strain hardening potential of the resulting SHMSHC. All results were compared with and benchmarked against the most studied PC-based PVA-SHCC M45 system.

[00150] Example 2B: Materials used under Example 2A

[00151] MgO used in this example was obtained from RBH Ltd. (United Kingdom). The undensified (U940) microsilica (MS) from Elkem Ltd. (Singapore) was used as the amorphous silica (SiO₂) source to prepare the SHMSHC. CEM I 42.5 N PC was used to prepare the control SHCC (M45) in this example. In the SHCC M45 mix, class F fly ash from Bisley Asia Pte. Ltd. (Singapore) and micro silica sand with an average size of 110 µm were also used. The chemical compositions and properties of MgO, MS, PC and fly ash are presented in FIG. 3. Sodium hexametaphosphate (SHMP) obtained from VWR Ltd. (Singapore) and polycarboxylate based high range water reducer (HRWR) were used as superplasticizers in SHMSHC and SHCC M45, respectively. The effectiveness of the two superplasticizers used within the corresponding systems has been demonstrated before. Short PVA microfibers from Kuraray Ltd. (Japan) were used at an amount of 2% by volume in both the SHMSHC and the SHCC M45 mixes. To determine the weight of the fibers to be incorporated in the mix, the total volume of the batch was multiplied by the density of the fibers. The properties of PVA fibers are shown in Table 2. The mix design details of SHMSHC and SHCC M45 are presented in Table 3. The exact mix design for SHCC M45 has been utilized previously in several SHCC studies. Similarly, the mix design involving M-S-H matrix with use of MgO:SiO₂ with 50:50 weight ratio has been used in several studies, however without

the use of any fibers. This study adopts the usage of PVA fibers 2% by volume and incorporates it into a M-S-H based matrix to obtain SHMSHC.

[00152] Example 2C: Sample Preparation under Example 2A

[00153] Preparation of SHMSHC samples that were used for tension and compression tests started with dissolving SHMP in the pre-determined amount of water. The dissolving process of SHMP took about 30 mins, during which external shaking or stirring was not required. Once the SHMP solution was ready, MgO powder was added into the solution and mixed using a Hobart HL200 planetary mixer for 3 mins. Afterwards, MS powder was incrementally added into the mixing bowl while stirring to avoid the formation of any clumps. After all MS powder was added, the mixing process continued for another 5 mins to ensure a homogenous mix was obtained. Lastly, the PVA fibers were added slowly into the mixing bowl to ensure they were well-dispersed. Afterwards, the fresh mixture was poured into dogbone-shaped moulds and 50 mm cubic moulds in preparation for the tensile and compressive tests, respectively. The dimensions of the dogbone samples that are used for tensile tests had a 36 mm (W) by 12 mm (D) cross-section in the middle portion while the total length of the samples were 350 mm.

[00154] To prepare SHCC M45, the high range water reducer was first dissolved in water. The binder mix involving PC, fly ash and silica sand were dry-mixed inside a Hobart planetary mixer for 2 mins until all the solids were homogeneously mixed. The superplasticizer solution was added into the dry mix and the mixing procedure continued for another 5 mins. Once the solid and liquid parts were thoroughly mixed, the PVA fibers were gradually added into the mix and the mixing procedure continued until all the fibers were well dispersed into the mix. SHMSHC and SHCC matrix mixtures (i.e. without the inclusion of PVA fibers) were also prepared to assess matrix fracture toughness by three point bending test and single fiber pull out test. For three point bending test samples, the fresh matrix mixtures were cast into 25 (B) × 50 (H) × 240 (L) mm prism moulds. A notch (a) with notch height-to-sample height (a/H) ratio of 0.4 was created in the middle of the prism by a diamond saw. To investigate the fiber/matrix interface properties, single fiber pull-out test specimens were prepared. These samples involved a single fiber embedded into the fresh matrix with one side of the fiber perpendicularly protruding out the matrix. The details of the preparation of

samples for the single fiber pull out test is described in example 3C below. All samples were cured under 28 ± 2 °C and $95 \pm 3\%$ relative humidity (RH) for 28 days.

[00155] Example 2D: Characterization of compression and uniaxial tensile tests under Example 2A

5 [00156] Load controlled compression tests were performed on 50 mm cube samples to determine the compressive strengths of SHMSHC and SHCC samples by using a Toni Technik Baustoffprüfsysteme machine. A constant loading rate of 55 kN/min was applied, after which the peak load was recorded. At least three samples were tested and the average compressive strength and standard deviations were reported for each data
10 point.

[00157] Uniaxial tensile tests under displacement control were carried out to quantify the tensile stress-strain behavior of SHMSHC and SHCC M45 dogbone samples via a 50 kN Instron 5569 universal testing machine (UTM). The deformation rate for the uniaxial tensile tests was 0.5 mm/min. The displacement over the middle section of
15 dogbone shaped samples was recorded by linear variable displacement transducers (LVDTs) attached on the two sides of the dogbone samples and the average of the two LVDT readings were taken as the displacement. At least three samples were tested and recorded for each data point.

20 **[00158] Example 2E: Characterization of Fracture surface and damage pattern characterization under Example 2A**

[00159] After the uniaxial tensile tests, fracture surface and damage pattern (i.e. residual crack width distribution, average residual crack width, average crack spacing) of unloaded specimens were characterized using a Nikon DS-Fi2 high resolution CCD camera equipped with high magnification lenses (OPTEM Zoom 70XL). Post image
25 process and analysis was carried out by means of an imaging software (NIS-Elements) by Nikon to measure the surface crack width along the centerline of the dog bone samples. The average crack spacing for each composite was determined by dividing the gauge length to the number of residual cracks. The field emission scanning electron microscopy (FESEM) images were taken via JEOL JSM-7600F instrument. The
30 accelerating voltage for FESEM was 5.0 kV. Prior to FESEM, the samples were coated with platinum under 20 mA current for 30 s.

[00160] Example 2F: Characterization of single fiber pull-out test under Example 2A

[00161] FIG. 4 shows the test setup of the single fiber pull-out test. The thin plate specimen was glue-fixed on a metal plate mounted to the 10 N load cell. The glue was only applied at the four corners of the thin plate specimen to ensure the fiber at the center of the bottom side of the specimen did not bond the metal plate. The protruded end of the fiber was glue-fixed to another metal plate clamp-fixed to the actuator of a MTS Acumen 1 Electrodynamic Test System. With the help of a precise adjustable x-y table that lies under the load cell, the position of the sample was carefully adjusted so that the fiber can be pulled out in a vertical orientation. The fiber was pulled out at a constant rate of 0.5 mm/min. Load versus displacement data were recorded. FIG. 5 shows a representative single PVA fiber pull-out curve of PC matrix. In the debonding stage, the pull-out load increases up to P_a . After which, a sudden load drop to P_b is observed due to complete debonding. This moment marks the end of the fiber debonding stage and the beginning of the fiber slippage stage. In the fiber debonding stage, the pull-out force P is counter-balanced by the chemical bond G_d at the bonded portion of the fiber, together with the interface frictional bond τ_0 at the debonded portion. After full debonding, the pull-out behavior is determined by only the frictional bond. During the fiber slippage stage, the soft fiber is likely to wear out due to the abrasion while slipping inside the hard matrix. This abrasion results in increased frictional forces which is referred as slip hardening, and the slip hardening coefficient β is determined by the slope of the curve at slippage stage. Accordingly, the interface chemical bond G_d , interface frictional bond τ_0 , and slip hardening coefficient β can be determined from the single fiber pull-out tests using the equations (3)–(5), where E_f is the fiber Young's modulus, d_f is the fiber diameter, L_e is the fiber embedment length, u' is the fiber displacement after debonding, $\Delta P/\Delta u'$ is the initial slope of the P versus u curve (u' approaches zero as seen in equation (5)).

$$G_d = \frac{2(P_a - P_b)^2}{\pi^2 E_f d_f^3} \quad (3)$$

$$\tau_0 = \frac{P_b}{\pi d_f L_c} \quad (4)$$

$$\beta = \frac{d_f}{L_g} \left(1 + \frac{1}{\pi \tau_0 d_f} \left. \frac{\Delta P}{\Delta u} \right|_{u' \rightarrow 0} \right) \quad (5)$$

[00162] Example 2G: Characterization of nano-indentation tests under Example 2A

[00163] To investigate mechanical properties of M-S-H and M45 matrices, nano-indentation tests were carried out using a Micro Materials Nanotest Vantage instrument fitted with a Berkovich tip. Matrix sample collected after the single fiber pull-out test was used as the specimen for nano-indentation tests. Prior to nano-indentation test, to obtain a smooth surface suitable for nano-indentation, samples were grinded, polished, and cleaned in isopropanol solution using a sonicator. For grinding and polishing processes, a rotary machine facing downward, and an adjustable precise z-axis stage was used. The sample glued to a perspex plate was fixed on the stage and the rotary machine was used to rotate a lapping wheel with abrasive paper attached. While the abrasive media was rotating, the height of the stage was carefully adjusted just high enough for sample to contact the abrasive paper in order to minimize the normal force, which can cause stress concentration on sample. For grinding, P1200 and P2500 grit abrasive papers were used; and grinding process was performed at several steps with each step being maximum 5 s to avoid formation of scratches. In between each step of grinding, an optical microscope was used to observe the evolution of the surface morphology of the sample. After grinding, the sample was cleaned in isopropanol solution using a sonicator. After the sample was cleaned, polishing was performed using the same setup, while instead of the abrasive paper, a synthetic silk polishing cloth charged with 1 μ m diamond paste was used. Additionally, 1:1 ratio mix of ethanol and 1.4 butanediol solution was applied on the polishing cloth to avoid over heating. In a similar fashion to grinding, the height of z-axis stage was adjusted to contact the surface of the specimen and the polishing was carried out up to 5 s. After polishing, the sample was once again cleaned using sonicator for 1 min.

[00164] A grid of indents was made with a spacing of 20 μm between each indent over an area of 0.0064 and 0.018 mm^2 on M-S-H and M45 matrixes, respectively. The maximum indentation depth was set to be 1 μm . The indentation modulus and indentation hardness for each indent was obtained from the software which used a polynomial function to calculate the modulus and hardness values from loading and unloading curves. In total, 25 indents for SHMSHC specimen and 60 indents for SHCC M45 specimen were produced. More number of indents were chosen to be implemented on SHCC M45 matrix due to the presence of micro silica sand in its mix composition. The indents occurred on micro silica sand particles (determined by microscopy observations) were excluded during data analyses for SHCC M45 matrix. The indentation modulus and the indentation hardness values were statistically evaluated to determine their average and standard deviation values for both SHMSHC and SHCC M45 matrices.

[00165] **Example 2H: Characterization of three point bending test under Example 2A**

[00166] Three point bending tests on notched prism specimens were performed to determine the fracture toughness of SHMSHC and SHCC matrixes. The prism specimen was placed on two line supports with a span of 200 mm. A line load with a constant displacement rate of 0.5 mm/min was applied at the middle of the span. The tests were carried out using a 50 kN Instron 5569 UTM in accordance with ASTM E399-12. The fracture toughness K_m was determined by equations (6)–(8), where $P_{\max}$ is the peak load, S is the loading span length, b is the width of the beam, d is the depth of the beam, a_l is the notch length.

$$K_m = \frac{3P_{\max}S}{2bd} \sqrt{\pi a_l} F(x) \quad (6)$$

$$F(x) = \frac{1}{\sqrt{\pi}} \frac{1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)}{(1+2x)(1-x)^{3/2}} \quad (7)$$

$$x = \frac{a_l}{d} \quad (8)$$

[00167] Example 2I: Characterization of micromechanics-based modelling for fiber bridging behavior and strain hardening potential assessment under Example 2A

[00168] The fiber bridging behavior, i.e., stress-crack opening relationship $\sigma(\delta)$ as shown FIG. 6, which governs the multiple cracking and strain hardening of SHCC, can be derived analytically based on micromechanical parameters obtained from the above tests. A numerical approach was used to calculate the fiber bridging curves of the SHMSHC and compared with SHCC M45. Once the fiber bridging curve is obtained, pseudo strain hardening (PSH) indices, which are often used to assess strain hardening potential of the fiber reinforced composites, can be determined according to equations (9)–(11), where σ_0 is the peak bridging stress, σ_c is the matrix tensile cracking strength, J'_b is the complementary energy calculated from the fiber bridging curve, J_{tip} is the crack tip toughness. For small fiber volumes, J_{tip} can be expressed as a function of the matrix fracture toughness K_m , and Young's modulus of matrix E_m , using equation (11). Composites with larger PSH indices should have better chance of saturated multiple cracking and thus robust strain hardening performance.

$$PSH_{Energy} = J'_b / J_{tip} \quad (9)$$

$$PSH_{Strength} = \sigma_0 / \sigma_c \quad (10)$$

$$J_{tip} = K_m^2 / E_m \quad (11)$$

[00169] Example 2J: Discussion on results of mechanical properties under Example 2A

[00170] FIG. 7 shows the tensile stress-strain curves and FIG. 8 summarizes the mechanical properties of SHMSHC and SHCC M45. As can be seen, both SHMSHC and SHCC M45 exhibit tensile strain hardening behavior with more than 2% tensile strain capacity on average, even though one sample from each mix was below 2%. It should be noted that the SHCC M45 specimen had similar performances with one another, meanwhile the differences between the performances of SHMSHC specimen were more pronounced. While the two mixes have comparable 28-day compressive strengths (i.e., 54.3 ± 0.5 MPa for SHMSHC and 53.6 ± 2.7 MPa for SHCC M45), the matrix first cracking strength of SHCC M45 (3.49 ± 0.57 MPa) under tension is about

81% higher than that of SHMSHC (1.93 ± 0.12 MPa). This suggests the SHMSHC matrix may be more brittle than the SHCC M45 matrix as increased brittleness results in reduced cracking resistance and strength. The ratio of average compressive strength to average matrix tensile strength for SHCC M45 and SHMSHC are 13.7 and 28.2, respectively, highlighting the brittle nature of M-S-H matrix. Further increase in the tensile load results in strain hardening behavior for both composites, reaching to strain capacities of $3.11 \pm 1.76\%$ and $2.48 \pm 0.73\%$ for the SHMSHC and SHCC M45, respectively. Accordingly, the SHMSHC possesses a lower average tensile strength (2.93 ± 0.64 MPa) than the SHCC M45 (3.72 ± 0.26 MPa), even though the relatively larger standard deviations hinder a firm conclusion. The observation suggests SHMSHC may have lower fiber bridging capacity than the SHCC M45 as the tensile strength of the composite is largely determined by its fiber bridging properties. FIG. 9A and 9B compare the morphology of fracture surfaces of SHMSHC and SHCC M45 specimens after the uniaxial tensile test. It was observed that there were several long fibers stuck out of the fracture surface of SHMSHC specimen (FIG. 9A) indicating at least a considerable proportion of fibers were pulled out from the M-S-H matrix, while a mixed fiber pull-out and fiber rupture were found in the SHCC M45 specimens (FIG. 9B). This suggests the bond between the PVA fiber and the M-S-H matrix is weaker than that between the PVA fiber and the M45 matrix, which results in potentially lower fiber bridging strength in the SHMSHC system.

[00171] Example 2K: Discussion on Results of damage pattern under Example 2A

[00172] While both SHMSHC and SHCC M45 have tensile strain capacity in excess of 2%, their damage patterns are very different. FIG. 10A and 10B show the visual appeals of cracked SHCC M45 and SHMSHC specimens after the tensile tests. For SHCC M45, multiple cracks were easily observed with naked human eyes. However, hardly any cracks were noticeable when the SHMSHC specimens were examined even under microscope with low magnification. Multiple cracks in SHMSHC were revealed under high magnification using optical microscope or under FESEM as shown in FIG. 11A and 11B. The multiple cracks formed in the SHMSHC specimens were very dense and the residual crack width (i.e. crack width after unloading) was generally less than 10 μm , making majority of the cracks unobservable unless the sample was examined

under microscope using a sufficient level of magnification. The average crack spacing (1.3 mm) in the SHMSHC is much smaller than that in the SHCC M45 (2.5 mm).

[00173] FIG. 12 compares the residual crack width distributions of SHMSHC and SHCC M45 and FIG. 13 summarizes the average residual crack width and crack spacing of the two mixes. As can be seen, majority of the cracks in SHMSHC were condensed in narrow crack width ranges, while cracks within SHCC M45 were more evenly distributed over the different width ranges. For instance, around $72 \pm 11\%$ of cracks were below $10 \mu\text{m}$ and $93 \pm 15\%$ of cracks were below $20 \mu\text{m}$ for SHMSHC, while distribution of cracks in the $<10 \mu\text{m}$ and between 10 and $20 \mu\text{m}$ ranges for SHCC M45 were $19 \pm 18\%$ and $22 \pm 10\%$, respectively. Additionally, more than 11% of the cracks in SHCC M45 were in the relatively larger crack width ranges such as $>50 \mu\text{m}$, meanwhile only 1% of the cracks in SHMSHC were larger than $50 \mu\text{m}$. As a result of the above-mentioned crack width distributions, the average residual crack width of the SHMSHC ($9.7 \mu\text{m}$) was much smaller than that of the SHCC M45 ($31.4 \mu\text{m}$). This suggests that cracked SHMSHC may possess lower transport properties when compared to cracked SHCC M45. Furthermore, it implies that SHMSHC may present higher chances of engaging autogenous healing, as cracks with tighter widths have better chances of being healed faster and completely as opposed to larger cracks.

[00174] **Example 2L: Discussion on results of fiber/matrix interface properties under Example 2A**

[00175] FIG. 14 compares typical single fiber pull-out curves of 1.2% surface oil-coated PVA fibers from the M-S-H and PC matrices and FIG. 15 summarizes the calculated interface chemical bond G_d , interface frictional bond τ_0 , and slip hardening coefficient β . Even though the pull-out load and displacement values for the two curves representing single fiber pull-out behavior of SHMSHC and SHCC M45 notably differ, these two curves have certain resemblance. As can be seen, both curves show a clear debonding stage followed by a slippage stage. This indicates surfaces of PVA fibers chemically react and bond with both the PC and the M-S-H matrices. It is known that PVA fibers are hydrophilic due to the presence of hydroxyl (OH^-) functional groups on the fiber surface. The hydroxyl functional groups on the fiber surfaces are able to chemically bond with Ca^{2+} in the PC matrix and similarly with Mg^{2+} in the M-S-H matrix. However, the interface chemical bond G_d for SHMSHC was 43% less than that

of SHCC M45 (FIG. 15). The lower interface chemical bond G_d in SHMSHC might be attributed to less abundance of available Mg^{2+} ions in comparison to Ca^{2+} ions to chemically bond with the OH^- functional groups on the fibers. It is known that solubility of brucite is three orders of magnitude lower than that of portlandite. Furthermore, Mg-OH may have a lower bond energy than Ca-OH as the entropy of brucite was reported to be about 5% lower than that of portlandite.

[00176] While the two systems had similar fiber debonding behaviour, the single fiber pull-out curves showed significant differences in the fiber slippage stage. As can be seen in FIG. 14, when a single fiber was pulled out from the M45 matrix, the load picked up sharply after full debonding of fiber from the surrounding matrix. In the M-S-H system, however, after the breaking of the chemical bonds, the pull-out load decreased slightly and gradually picked up after a long fiber slippage (around 0.5 mm as shown in FIG. 14). In the current example, two slip hardening coefficients (i.e. initial slip hardening coefficient β_1 and second slip hardening coefficient β_2) were used to describe the delayed slip hardening in the M-S-H system while only the initial slip hardening coefficient was used for the M45 matrix.

[00177] Slip hardening in single fiber pull-out behaviour is often observed in the soft fiber and hard matrix system and is associated with abrasion of soft fiber due to fiber slippage against surrounding hard matrix. Accumulation of fiber debris in the tunnel (i.e. space between debonded fiber and surrounding matrix) makes fiber slippage more difficult (i.e., jamming effect) and thus a higher load is necessary to further pull out the fiber.

[00178] The significantly delayed slip hardening behaviour in the M-S-H matrix may be an indication of lower abrasion of the PVA fibers within the M-S-H matrix during the early periods of pull-out stage. This may be attributed to the following three mechanisms. First, the lower interface chemical bond G_d between PVA fibers and M-S-H matrix allows the tunnel crack to propagate along the interface without branching into the fiber or the surrounding matrix, and thus resulting in a smooth debonded interface. FIG. 16 shows the typical fiber groove after the PVA fiber was pulled out from the M-S-H matrix. As can be seen, a rather smooth morphology of the fiber groove without indications of debris accumulation was observed in the M-S-H system. Secondly, the M-S-H matrix may have a lower modulus than the PC matrix, and thus

resulting a lower gripping force to the fiber from the surrounding M-S-H matrix. Thirdly, the M-S-H matrix may be softer than the PC matrix. All of these mechanisms may lead to less abrasion of PVA fibers and delayed slip hardening in the M-S-H system. [00179] Overall, the bonding behaviour is influenced by several parameters including fiber properties (e.g. length, diameter, volume, Young's modulus, tensile strength), matrix properties (i.e. modulus of elasticity, cracking strength, matrix toughness) as well as the fiber/matrix interface properties (i.e. G_d , τ_0 , β , f , f'). Further studies can help to better understand and improve the bonding between fibers and the newly introduced M-S-H matrix.

10 **[00180] Example 2M: Discussion on results of matrix properties under Example 2A**

[00181] SHMSHC and SHCC M45 matrix properties in terms of indentation modulus and hardness measured from the nano-indentation tests and fracture toughness determined from the three-point bending test on notched specimens are reported in FIG. 17. FIG. 18 shows the indentation modulus and indentation hardness values of indents on SHMSHC and SHCC M45 specimens. As can be seen, vast majority of the indents on SHMSHC matrix had lower indentation modulus values in comparison to indents on SHCC M45 matrix. The average indentation hardness (H) for M-S-H matrix was 1.04 ± 0.27 GPa, which was around 37% lower than the average indentation hardness value of 1.66 ± 0.54 GPa for the SHCC M45 matrix. The average hardness value for SHCC M45 matrix was similar with one reported earlier (i.e. 1.78 GPa). As discussed in the previous example, the lower average hardness of the M-S-H matrix can potentially reduce abrasion of PVA fiber and delay the slip hardening during the fiber slippage stage as shown in FIG. 14.

25 [00182] The indentation modulus (M) of M-S-H matrix was found out to be 21.07 ± 3.76 GPa, which was 49% lower than the indentation modulus value of 41.6 GPa for SHCC M45. Similar indentation modulus of SHCC M45 matrix was reported (i.e. 43.2 GPa). As discussed, the lower indentation modulus of the M-S-H matrix could induce less gripping force to the fiber from the surrounding matrix which also reduces abrasion of PVA fiber and delays slip hardening (FIG. 14).

30 [00183] As can be seen from FIG. 17, toughness of SHMSHC matrix (0.45 ± 0.17 J/m²) determined from the notched beam bending tests was much lower than that of SHCC

45 matrix ($2.89 \pm 0.64 \text{ J/m}^2$). This indicates that the M-S-H matrix was much more brittle than the SHCC M45 matrix (FIG. 8). The higher brittleness of the M-S-H matrix results in a lower matrix cracking strength under tension as observed in the composite test (FIG. 7 and FIG. 8). The crack tip toughness J_{tip} can be then calculated using
 5 equation (11). In the current study, the indentation modulus (instead of the bulk matrix modulus of elasticity) was used as the input (E_m) for the calculation of crack tip toughness J_{tip} . Young's modulus determined from macro-scale testing (such as compression test) is a bulk material property and is influenced by macro-defects in the matrix, while the elastic modulus obtained from nano-indentation tests is a localized
 10 material property. Since the crack tip toughness is governed by the localized material properties around the crack tip, indentation modulus should better reflect the modulus of elasticity for crack tip toughness calculations.

[00184] Example 2N: Discussion on results of meso-scale characterization: fiber bridging analysis and strain hardening potential assessment under Example 2A

15 **[00185]** The fiber bridging behavior of SHMSHC and SHCC M45 can be calculated based on the measured micromechanical parameters as summarized in FIG. 19. The resulting fiber bridging curves for both SHMSHC and SHCC M45 are plotted in FIG. 21. Compared to SHCC M45, SHMSHC possesses lower bridging strength perhaps due to the lower initial slip hardening coefficient β_1 which results in minimum slip
 20 hardening after fiber debonding. Furthermore, after the first peak, the bridging stress reduces first and then maintains at a certain stress level with increasing crack opening. This may be attributed to the long sliding before entering the hardening stage (i.e. delayed slip hardening) as observed in the single fiber pull-out test of SHMSHC (FIG. 14). As can be seen in FIG. 21, the crack opening corresponding to first cracking
 25 strength for SHMSHC is smaller than that of SHCC M45, which is line with the actual crack width values discussed in example 2K.

[00186] FIG. 20 summarizes J_b' , J_{tip} , σ_0 , and σ_c values and corresponding PSH indices of SHMSHC and SHCC M45. As can be seen, both SHMSHC and SHCC M45 possess PSH indices larger than one. This suggests both materials satisfy criteria of achieving
 30 the strain hardening performance. However, large margins between J_b' and J_{tip} and between σ_0 and σ_c are often necessary to accommodate expected variability and inhomogeneity of the material. SHMSHC possesses much higher values of PSH

indices, which suggests it has a much higher strain hardening potential and chances of forming saturated multiple cracking than SHCC M45. Furthermore, with lower toughness and cracking strength of M-S-H matrix under tension and comparable stiffness of the fiber bridging to SHCC M45 before the peak bridging stress, multiple cracks in SHMSHC would initiate and propagate in a steady state mode at a much lower stress level (FIG. 21 inset), which results in tighter crack width and closer crack spacing in SHMSHC as shown in the composite tensile tests (FIG. 8).

[00187] Example 2O: Summary of discussion under Example 2A

[00188] In examples 2A to 2O, the present SHMSHC was demonstrated by incorporating, as a non-limiting example, 2 vol% short and randomly oriented PVA microfibers. The resulting SHMSHC exhibits remarkable strain hardening under tension with a tensile strain capacity of more than 3%, a compressive strength beyond 50 MPa, and a tensile strength of around 3 MPa. While SHMSHC and SHCC M45 show comparable mechanical performance, they possess distinctive damage patterns where SHMSHC exhibits much tighter crack width (9.7 μm vs 31 μm) and closer crack spacing (1.3 mm vs 2.5 mm) invisible to the human naked eyes. This is attributed to the lower toughness and cracking strength of M-S-H matrix together with higher PSH indices, and thus saturated multiple cracks could initiate and propagate at a much lower stress level in SHMSHC. Furthermore, average chemical debonding between PVA fiber and M-S-H matrix is significantly lower than that between PVA fiber and PC matrix (0.61 vs 1.08 J/m²). Slip hardening is significantly delayed when a single PVA fiber is pulled out from the M-S-H matrix, suggesting abrasion of PVA fiber during sliding against the M-S-H matrix is reduced due to lower hardness and modulus of the M-S-H matrix.

[00189] While M-S-H cement has emerged as an alternative cement with potentially lower energy requirements and emissions, its intrinsically low pH values makes incorporation of normal steel reinforcement not feasible. The presently developed SHMSHC addresses the fundamental challenge of M-S-H and is expected to widen possible application areas of M-S-H system. Furthermore, SHMSHC have great potential to be a sustainable alternative to PC based strain-hardening composites in certain applications. The industry significantly benefits from a bendable concrete with satisfactory mechanical properties and lower environmental impact. A challenge for

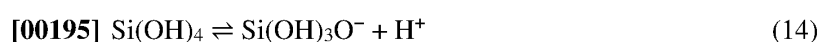
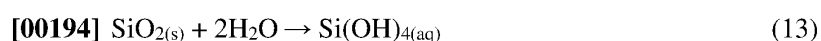
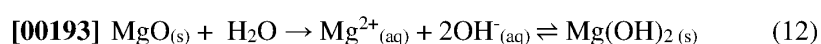
SHMSHC could be considered as relatively low ultimate tensile strengths reached, which can be attributed to the intrinsically low matrix cracking toughness. Further investigations can focus on the improvement of SHMSHC properties via microstructure optimization by means of component tailoring and ingredients selection. Additionally, life cycle analysis (LCA) and life cycle cost analysis (LCCA) would provide a clearer picture on the feasibility and environmental impact of SHMSHC.

[00190] Example 3A: Overview on use of polyethylene (PE) microfibers in reduced amounts to obtain cost effective high-performance strain-hardening magnesium-silicate-hydrate composites (SHMSHC)

[00191] In addition to significantly contributing to global carbon dioxide (CO₂) emissions, production of Portland cement (PC) requires heating up to high temperatures (i.e. 1450°C) and hence it is also energy intensive. There is a demand for alternative cementitious binders that can replace PC at least in certain applications. Magnesium oxide (MgO) based cements may provide an environmentally friendly alternative to PC due to lower calcination temperature requirement of magnesite (MgCO₃) and potentially lower associated net-CO₂ emissions, due to the ability of carbonated MgO-based cement to capture and store CO₂. In addition to by calcination of magnesite at low temperatures (i.e. ~ >700°C), MgO can also be obtained from reject brine and magnesium-rich silicate rocks such as olivine ((Mg, Fe)₂SiO₄).

[00192] Magnesium-silicate-hydrate (M-S-H) cements belong to the family of MgO-based cements. The strength gaining mechanism of M-S-H cements is hydration and therefore curing of this system does not require accelerated CO₂ conditions like carbonated MgO systems. The formation of M-S-H takes places within the MgO-SiO₂-H₂O system as follows. When MgO is in contact with water it dissolves into Mg²⁺ and OH⁻ ions, and when a saturation level is reached (pH=10.5) precipitation of Mg(OH)₂ (brucite) takes place as shown in equation 12 below. Introduction of silica (SiO₂) into the systems results in formation of orthosilicic acid (Si(OH)₄), which dissociates to form silicate ions as shown in equations 13 and 14 below, respectively. Under room temperature and neutral pH levels dissolution of silica is very limited however alkaline environment facilitates the dissolution of silica. The reaction of magnesium and silica ions in the pore solutions leads to formation of M-S-H, which is responsible for strength gain in the MgO-SiO₂-H₂O system. Within this system sodium hexametaphosphate

(SHMP) is often used as a superplasticizer. In addition to helping to reduce water content, SHMP plays a significant role in enhancing the formation of M-S-H. Presence of SHMP increases the pH of the solution thereby increasing the dissolution of SiO₂. Furthermore, SHMP was found to inhibit formation of Mg(OH)₂, which reduces the competition for Mg²⁺ ions for silicate species, favoring the formation M-S-H as opposed to brucite.



[00196] Strain hardening cementitious composites (SHCCs) refer to cement-based composites that can undergo notable tensile ductility at low fiber dosages (e.g. ≤2% by volume). Conventional concrete exhibits quasi-brittle failure under tension and SHHCs are developed to address the undesirable brittleness of concrete. SHCC can exhibit several hundred times better ductility in comparison to conventional concrete. The characteristics that make SHCCs unique include high tensile ductility and formation of multiple tight cracks (generally below 100 μm in width). Micromechanics-based principles that takes into account the fiber, matrix and fiber/matrix bond properties to determine fiber-bridging curves, are used for the careful design of SHCCs.

[00197] M-S-H matrix has intrinsically low pH values (i.e.~10.0-10.5). The reinforcement steel passivation requires much higher pH than the final pore solution pH of M-S-H; therefore steel reinforcement is not possible for M-S-H matrix, limiting its applications. Reinforcement using polymeric microfibers can be a good alternative to improve the flexural and tensile performance of SHMSHC. As demonstrated in examples 2A to 2O, strain-hardening magnesium-silicate-hydrate composites (SHMSHC) were developed using polyvinyl alcohol (PVA) fibers. The developed composites had strain capacities exceeding 3% with inclusion of 2% by volume PVA fibers. The examples noted significantly high pseudo strain-hardening (PSH) indices for SHMSHC in comparison to PC-based composites, which was attributed to low matrix cracking toughness of M-S-H matrix.

[00198] In SHCC majority of costs originate from fiber prices even though fibers are used at much lower amounts in comparison to binder. Therefore, lowering the fiber content in SHCC can lead to significant reduction of the overall costs. In this study,

SHMSHC with lowered PE fiber contents were developed. The tensile performance of composites at various PE fiber dosages were investigated. The damage pattern and fracture surface of each mix was investigated via microscopy. Single-fiber pullout tests were performed to investigate the bonding behavior between PE fibers and M-S-H matrix. Lastly, micromechanics-based modelling was used to explain the obtained fiber bridging behavior with the given parameters.

[00199] Example 3B: Materials used under Example 3A

[00200] MgO used in this research was supplied by RBH Ltd. (United Kingdom). The other constituent of the binder phase was undensified (U940) microsilica (MS) from Elkem Ltd. (Singapore). The chemical compositions of MgO and MS as obtained from the suppliers are presented in Table 2 below. To improve the workability of the mixes sodium hexametaphosphate (SHMP) obtained from VWR Ltd. (Singapore) was used in the mixing process. Honeywell Spectra® 1000 PE microfibers, whose properties are shown in Table 3, were used in SHMSHC mixes at four different amounts, that were 0.25, 0.50, 1.00 and 2.00% by volume of fiber. The mix compositions of SHMSHC with PE fibers can be seen in Table 4.

[00201] Table 2 - Chemical composition of MgO, MS (as obtained from suppliers).

Material	MgO	CaO	SiO ₂	Al ₂ O ₃	R ₂ O ₃	K ₂ O	Na ₂ O
MgO	>91.5%	1.6%	2.0%	<0.7%	-	-	-
MS	-	-	>90.0%	-	-	-	-

[00202] Table 3 - Properties of the PE fibers (as obtained from supplier).

Length (mm)	Diameter (μm)	Elastic Modulus (GPa)	Density (kg/m ³)	Nominal tensile strength (MPa)
19	23	113	960	3250

[00203] Table 4 - Mix design of the SHMSHC.

Sample	MgO (wt.%)	MS (wt.%)	w/b	SHMP (wt.% of total binder)	PE fiber content (vol.%)
SHMSHC	50	50	0.45	2.0%	2, 1, 0.5 or 0.25

[00204] Example 3C: Sample preparation under Example 3A

[00205] For mix preparation the first step was dissolving the SHMP in the mixing water. The dissolving of the flakes took around 30 mins and external mixing was not necessary for this procedure. When the superplasticizer solution was ready, it was added into a Hobart HL200 planetary mixer and firstly mixed with the MgO powder.

5 Afterwards microsilica powder was added in multiple steps while mixing continued. The microsilica powder was not added in a single step to avoid agglomeration and trapping of water. After a homogenous paste mix was obtained PE fibers were added into the mix in a gradual manner to ensure the fibers are well dispersed into the mix. After the mix was ready, the mix was poured into 50 mm cubic and dogbone-shaped

10 moulds for preparation of the samples for compressive and tensile testing, respectively. The dogbone-shaped samples had a cross section of 36 mm (width) by 12 mm (depth) in the middle part and the total length of the samples were 350 mm.

[00206] Single fiber pull-out test specimens were prepared to investigate the bond properties between PE fibers and M-S-H matrix. Same paste mix with the composite

15 samples, however without the inclusion of microfibers, was used in preparation of single-fiber pullout test specimen. FIG. 22 shows the details of the samples prepared for the single fiber pull out tests. At the end of the curing period the 40 by 60 mm rectangular samples were cut using a diamond saw along the dashed lines shown in FIG. 22 to obtain small rectangular prisms with a single fiber protruding out of the

20 matrix served as the single fiber pull-out specimen. Both composite and single fiber pull-out specimens were cured for 28 days under $28\pm 2^{\circ}\text{C}$ and $95\pm 5\%$ relative humidity (RH) before being tested.

[00207] Example 3D: Characterization under Example 3A

[00208] Compression test and uniaxial tensile test are carried out as described in

25 example 2D. Fracture surface and damage pattern characterization was carried out as described in example 2E.

[00209] Single fiber pull-out test was carried out as described in example 2F. In this example, the load versus displacement data of more than 8 specimen were recorded. FIG. 23 shows two representative single fiber pull-out curves out from PC-based

30 matrix. Both curves belonged to PE fibers with one of the fibers being coated with carbon nano-fibers (CNF) to improve the fiber/matrix bond while the other PE fiber was uncoated. Regardless of the coating situation, PE fibers exhibited a similar pattern

under the single-fiber pullout test even though the CNF coated PE fiber performed better. In the earlier stages of the pull-out test, the pull-out load sharply increases up to P_{peak} , after which a gradual drop in the pullout load was observed while the displacement was increasing. This reduction in the pullout load is expected as the embedded length of the fiber reduces as pulling out proceeds. The increase in displacement continued until the fiber was fully pulled out of the matrix. In the single fiber pullout test with PE fibers, the pull-out load P is counter-balanced with the interface frictional bond τ_0 . Accordingly, the interface frictional bond τ_0 can be calculated using equation 15 below, where d_f is the diameter of fiber and L_e is the embedded length of fiber. Once the P_{peak} is reached, the pullout load always dropped and never showed an upward trend except for the negligible little noises in the plot.

$$\tau_0 = \frac{P_{\text{peak}}}{\pi d_f L_e} \quad (15)$$

[00210] Characterization by micromechanics-based modelling for fiber bridging behavior and strain hardening potential assessment is described in example 2I and FIG. 6.

[00211] **Example 3E: Discussion on mechanical properties under Example 3A**

[00212] FIG. 24A to 24D show the tensile stress-strain curves and FIG. 24E summarizes the mechanical properties of SHMSHC at different PE fiber dosages. As can be seen, SHMSHC exhibit tensile strain hardening behavior with more than 6% tensile strain capacity on average as long as the fiber dosage is 0.5 vol.% or above. The average first cracking strength of SHMSHC under tension was in the range of 0.5-0.7 MPa, while the compressive strength of specimen with different fiber dosages varied between 69.4-86.1 MPa. The significantly high ratio between the compressive strength and tensile strength of specimen indicates the high degree of brittleness of M-S-H matrix.

[00213] When the tensile strain capacities of the four different mixes are investigated, it is observed that the mixes with 2, 1, and 0.5 vol.% fiber dosages exhibited significant levels of average strain-hardening capacities of 6.33, 6.80 and 7.20%, respectively. This shows that M-S-H based composites has the capacity to utilize PE fibers at dosages as low as 0.5% and still exhibit high ductility. However, a slight reduction of the fiber dosage to 0.25 vol.% from 0.5 vol.% resulted in massively lowered ductility and load

carrying capacity, highlighting the importance of the careful mix design. One trend to notice in the tensile strain capacities of mixes with 2, 1, and 0.5 vol.% fiber dosages is that strain capacity of mixes were increased when the fiber dosage was reduced from 2 to 1% and from 1 to 0.5%. This initially sounds counter intuitive as higher fiber dosage is expected to provide a higher bridging force in the composites. However, a fiber content beyond the cement matrix can handle might result in inhomogeneous mixing of fibers, tangling of fibers, entrapping of extra air into the mix and these might adversely affect the workability of the mix in addition to introducing imperfections. These unfavorable effects were reflected also on the average compressive strength results of the composites with 2 and 1 vol.% fiber dosage (i.e. 69.4 and 72.9 MPa) in comparison to that of composites with 0.5 vol.% fiber dosage (i.e. 86.1 MPa).

[00214] When the ultimate tensile strengths of the composites with different fiber dosages are compared, it is observed that there is an increase in the ultimate tensile strength with the increase in fiber dosage with the exception of from 1 to 2 vol.% of fibers. This shows that at 2 vol.% there is excess amount of fiber and the fibers are not utilized effectively. A similar observation is valid when the composites with 0.5 and 1 vol.% fibers are compared. Even though there is an increase in the ultimate tensile strength for the composites with 1 vol.% fibers, the increase in comparison to 0.5% (around 44%) is not as high as expected. When the fiber amount is doubled (from 0.5 to 1 vol.%) the fiber bridging force is expected to be doubled as well. This suggests that even at 1 vol.% there is ineffective fiber utilization to some extent, while the average ultimate tensile strength was the highest (3.23 MPa) in comparison to other fiber dosages. At 0.25 vol.% fiber dosage, the ultimate tensile strength was further reduced to 1.41 MPa, accompanied with significantly lower average strain capacity (0.84%).

[00215] Example 3F: Discussion on damage pattern under Example 3A

[00216] FIG. 25A to 25D show the morphology of fracture surfaces of SHMSHC specimens with different fiber dosages after the uniaxial tensile tests. For all of the mixes, several fibers sticking out from the fracture surface was observed. This suggests a fiber pullout failure behavior for the composites irrespective of the fiber dosage. This observation shows that during tensile testing the ultimate tensile capacity of the PE fibers were not reached (even at low fiber dosages), but rather the samples have failed due to sliding of the fibers out from the matrix. An enhanced fiber/matrix bond might

be beneficial to improve the performance of SHMSHC with PE fibers. Additionally, it can be seen from FIG. 25A to 25D that the density of the fibers varies depending on the fiber dosages. Composites with 2 and 1 vol.% fiber dosages (FIG. 25A and 25B) show clusters of fibers stuck together at certain areas. This agglomeration of fibers results in ineffective utilization of fibers and lowered compressive and tensile performances as discussed in the previous example.

[00217] FIG. 26A to 26D show the images of cracked SHMSHC specimens at different fiber dosages after the tensile tests and FIG. 26E summarizes the corresponding residual average crack width and crack spacing of the specimen. At PE fiber dosages of 2% and 1% (FIG. 26A and 26B) formation of closely spaced thin cracks are observed. Accordingly, the residual average crack widths were 37.5 and 44.3 μm at 2% and 1% fiber dosages respectively, while both specimens had an average crack spacing of ~ 0.9 mm. When the fiber dosage was reduced to 0.5%, the average residual crack width increased to 73.5 μm and the cracks were more apparent on the specimen as can be seen from FIG. 26C. The increased average crack width was accompanied with a reduction in the number of cracks resulting in an average crack spacing of 1.80 mm for the specimen at 0.5% fiber dosage. Even though the crack spacing was reduced for 0.5% fiber dosage samples, overall strain-hardening performance was not compromised, as discussed in example 3E, which can be attributed to the formation of larger cracks. When the fiber dosage was further reduced to 0.25%, the residual average crack width was 54.8 μm , however the standard deviation was very large indicating formation of significantly larger cracks than the average value coupled with some significantly narrower cracks. Additionally, the average crack spacing was significantly increased to 4.6 mm from 0.9 mm for 1 and 2% fiber dosages, indicating more than 400% increase. The increased variation in crack widths and significantly larger crack spacing were also adversely reflected on the poor mechanical performance of the specimen with 0.25% fiber dosage.

[00218] Example 3G: Discussion on fiber/matrix interface properties under Example 3A

[00219] FIG. 27 shows a single fiber pull-out curve of PE fiber from the M-S-H matrix. The appearance of the curve significantly differs from single fiber pullout curve of a PE fiber out of PC matrix (presented in FIG. 23). When the PE fiber is pulled out of PC

matrix, once a peak load is reached, the axial load constantly reduces until the fiber is fully pulled out of the matrix and a further increase in the axial load is never observed after the peak load. However, when the PE fiber is pulled out of M-S-H matrix (FIG. 27), there are multiple zones of increase in the axial load resulting in several peaks in the axial load versus displacement plot. In other words, the plot resembles occurrence of several rounds of slip-hardening behaviour during the pull-out of a single fiber out of M-S-H matrix. The formation of multiple rounds of increase in pull-out load was repeatedly observed in all of the tested single-fiber pullout specimen albeit with various peak heights. The interface frictional force, τ_0 value was calculated as 0.83 taking the highest point of the first peak as P_{peak} . The occurrence of increased pullout load might be due to fiber getting stuck inside the groove while being pulled out of the matrix. In examples 2A to 2O, a delayed slip-hardening of PVA fiber pulled-out of M-S-H matrix was observed but it was not consisting of multiple rounds. Herein, multiple slip-hardening behavior of PE fibers is presently demonstrated.

[00220] FIG. 28A and 28B are FESEM images of extracted pieces taken from the fracture surfaces of dog-bone shaped composite samples after tensile testing. FIG. 28A shows a typical fiber groove consisting of several areas with indications of a fiber with bumps had been pulled out of the matrix. These areas with larger holes along the groove are highlighted with white dashed lines in the FIG. 28A, and similar morphologies are observed in many of the other fiber grooves. The existence of multiple bumps in the fiber groove are in line with observed single fiber pull-out behavior (FIG. 27) consisting of several rounds of slip-hardening. The presence of several bumps in the fiber might be due to strong gripping force exerted on the PE fibers, which are weak in radial direction, due to the shrinkage of the M-S-H matrix which is known to exhibit high levels of shrinkage. The tangling of the fibers during mixing might have created some nodes as well and contributed to the formation of bumps in composite samples. The existing nodes on fibers must have resulted in jamming of the fiber at multiple locations resulting in an increase of pull-out force, which was reflected in the high tensile performance of the samples at composite level. FIG. 28B shows formation of thicker areas on the fibers along with some indications of abrasion which might have contributed to fibers getting stuck inside the groove at some locations.

[00221] Example 3H: Discussion on results of fiber bridging analysis and strain hardening potential assessment under Example 3A

[00222] The fiber bridging behavior of SHMSHC can be calculated based on the measured micromechanical parameters as summarized in Table 5 below. This behaviour may be attributed to the long sliding before entering the hardening stage (i.e. delayed slip hardening) as observed in the single fiber pull-out test of SHMSHC (FIG. 27).

[00223] Table 5 - Micromechanical parameters of SHMSHC

Mix	Fiber					Interface					Matrix	
	E_f (GPa)	L_f (mm)	d_f (μ m)	σ_{fu} (MPa)	V_f (%)	f	f'	G_d (J/m ²)	τ_0 (MPa)	β	E_m (GPa)	K_m (MPa)
SHMSHC with PE fibers	113	19	23	3250	2 1 0.5 0.25	0.6 ^a	0.0 ^a	0	0.83	0	21	0.1

a: assumed value

[00224] Example 3I: Summary of discussion under example 3A

[00225] Microfibers constitute the majority of the costs in SHCC, therefore configuration of a SHCC with reduced fiber contents helps address the economic concerns of fiber reinforced concrete. In examples of 3A to 3I, the performances of SHMSHC prepared using PE fibers at various amounts were investigated. The composite level tensile and compressive test results were supported by analyses of failure surfaces and damage patterns via microcopy. Single fiber pull-out tests were conducted to investigate the bond between PE fiber and M-S-H matrix revealing an unconventional behavior. Lastly, micromechanics-based modelling was used to explain the different behaviors observed at various fiber dosages.

[00226] More than manageable incorporation of fibers causing workability concerns was found to be unfavorable for compressive strength of the samples, while all mixes had average 28-day compressive strength in excess of 69 MPa. The tensile test results showed that even at uncommonly low PE fiber contents such as 0.5% by vol., SHMSHC exhibit significant strain-hardening behavior reaching beyond 7% strain capacity. Fracture surface investigations suggested pullout of fibers in all samples regardless of the fiber dosage. For samples with 1.0-2.0 vol.% PE fibers very closely spaced cracks with an average crack spacing of less than 1 mm were observed. Single fiber pullout

tests showed a multistage slip-hardening behaviour which has not been observed before. The FESEM observations indicated possible formation of nodes on the fibers which potentially results in jamming of fibers during slippage inside the matrix. Micromechanics model suggested that 0.5 vol.% fibers is the lowest content that can satisfy both energy and strength criteria given the interface frictional bond (τ_0) value of 0.83. This observation was in line with the significantly reduced performance of composites with 0.25% fiber dosage in comparison to composites with 0.50% fiber dosage.

[00227] These examples showed that high ductility performance as well as satisfactory ultimate tensile strengths and high compressive strength of SHMSHC at low PE fiber dosages (e.g. 0.5-1.0 vol.%) can present a cost-effective solution for SHCC applications. Further studies can focus on reducing the binder content in the SHMSHC via inclusion of aggregates, which can further reduce the price of the composites.

[00228] **Example 4A: Overview of Low cost and low carbon footprint bendable concrete**

[00229] Due to the unsustainable carbon pollution from the manufacture of concrete, the present disclosure investigates the possibility of using magnesium-silicate-hydrate (M-S-H) based cement as an alternative cementitious material to Portland cement (PC) to reduce this environmental problem. Despite being one of the most commonly used construction materials worldwide, concrete has poor tensile properties. Thus, Engineered Cementitious Composites (ECC) has emerged as a replacement to conventional concrete. ECC has strain-hardening properties which are govern by fiber, cement matrix and interface properties.

[00230] This example focuses on the feasibility of using MSH-based cement with sand. Different proportion of silica sand and river sand were included in this example to reduce the cost of ECC while attaining desirable mechanical properties. The mechanical properties were investigated after 28 days of curing.

[00231] It can be observed that with the addition of silica sand and river sand in the composites, both composites demonstrated strain-hardening behaviour with multiple cracks observed and high compressive strength. Even though, the tensile strain-hardening capacity of the composites decreases as the sand/binder ratio increases, a

composite with a higher sand/binder ratio also displayed relatively desirable mechanical properties.

[00232] Example 4B: Materials and compositional configuration under Example 4A

5 **[00233]** In this example, the mix consists of cementitious materials, fine aggregates, superplasticiser and polyethylene (PE) fibers.

[00234] In the mix configuration, reactive magnesium oxide (MgO) cement provided by Richard Baker Harrison (UK) and micro silica (MS) obtained from Elkem Material (Singapore) acts as the main binder, designed to be 50-50 proportion by weight.

10 **[00235]** Two types of sand are used for this experiment. Fine silica sand obtained from Rock & Sand Industries (RSI) or river sand of particle size between 2.36 μm and 4.75 μm were used to reduce the cost of MSH concrete.

[00236] Sodium Hexametaphosphate (SHMP) obtained from VWR (Singapore) was used as a dispersant to improve its workability and it is kept constant at 2% of the total mass of binder for desirable results. With the inclusion of a superplasticiser, a water to binder ratio (w/b) of 0.4 was used. A lower water content can result in lower workability and mechanical properties obtained whereas, although a higher water content increases porosity and workability of concrete, it also results in a decrease in strength and increase likelihood of shrinkage occurring.

20 **[00237]** PE fiber of length 19mm (Spectra® Fiber 1000), obtained from Honeywell, helps to improve its mechanical properties. The use of a fiber of length 19 mm also ensures that their breaking strength are achieved before fully debonding from the matrix. The PE fibers were kept constant at 1% by volume, based on the mixes from studied in examples 3A to 3I conducted using different percentage (0.25%, 0.5%, 1%, 25 2%) of PE fibers added. The mix configurations are shown in FIG. 32.

[00238] Example 4C: Sample preparation under Example 4A

[00239] In this example, all the mixtures were prepared according to a standard mixing procedure as follows.

30 **[00240]** A shear-type Hobart mixer was used as shown in FIG. 34 (left image). Before casting, the mixing bowl should be cleaned before use by wiping with a damp cloth. All moulds used should also be cleaned (no hardened concrete residual at the inner side

of the mould), tightened (to prevent leakage of concrete) and oiled (to allow ease of demoulding).

[00241] The sample preparation process started with the addition of sodium hexametaphosphate (SHMP) crystals in the required amount of water into a bottle. The bottle was continuously shaken to ensure that all the crystals had dissolved (no visible crystals seen). The dissolved SHMP solution was then added to the MgO in the mixer. Upon obtaining a homogenous mixture, MS was added in small amounts continuously into the mixer to prevent lumps of MgO and Ms from forming. Sand was then added into the mix in small proportion to ensure uniform mixing. PE fibers were slowly added into the mixer at a lower speed to prevent breakage of fiber and lumping of fibers together.

[00242] The fresh mixture was casted into cubic moulds (50 x 50 x 50 mm²) and dog-boned moulds to determine compressive and tensile strength, respectively. When casting, manual compaction of cement is performed to ensure that there are no air holes in the cement. After casting, the moulds would be covered using a plastic sheet to prevent water from evaporating into the surroundings (as shown in FIG. 34 (right image)). The samples were demoulded the next day and left to cure in an enclosed box with moist condition for 28 days.

[00243] The workability of the mixes are to be measured after mixing. Once curing was completed, the mechanical properties of the samples are to be evaluated and the reasons behind their properties would be analysed via microscopic observations.

[00244] Example 4D: Characterization under Example 4A

[00245] The workability of the mixes would be measured by the average diameter of the flow spread on the flow table, taken across four different direction, after turning for 25 times as shown in FIG. 35.

[00246] For each mix design, compressive test was conducted on at least three cubes in accordance with the specifications of ASTM C109/C109M-13, at a loading rate of 55kN/min until failure of the cubes. This was done using Toni Technik Baustoffprüfsysteme machine. The compressive strength (maximum load) were recorded down.

[00247] Uniaxial tensile test was carried out on a minimum of 3 dog-boned samples using an Instron 5569, at a constant loading rate of 0.5 mm/min, to obtain the tensile

stress and strain of the samples. The specimens were tested till failure. Two Linear Variable Differential Transformers (LVDTs) were attached to the specimens, secured using mechanical grips. The tensile strain of the specimens was calculated from the average displacement of the gauged length of the LVDTs.

5 [00248] Crack patterns for each mix such as the number of cracks, average crack width and crack spacing within the gauged length are investigated after the uniaxial test. These crack patterns are captured using a Nikon DS-Fi2 high resolution camera equipped with NIS Elements (Nikon) software which is then amplified through an OPTEM Zoom 70XL microscope with a magnifying rate of 420 times.

10 [00249] For FESEM imaging, the samples were prepared using IsoMet 4000 at a blade speed of 4000 rpm and a feed rate of 10.1 mm/min. For each batch, a section of the dog-boned specimen would be obtained. The first cut were done near the edge while the second cut was made about 1 cm from the first cut. After which, 3 separate cuts were made of about 0.5 cm each to obtain the samples. This procedure is depicted using an
15 enlarged section of a specimen, as seen in FIG. 36. These samples were left to dry in an oven for more than 24 hours.

[00250] Before testing, the samples were coated using JEOL JFC-16000 and observed under Field Emission Scanning Electron Microscope (FSEM) to determine the method of crack propagation (if the cracks propagate across or around the aggregates).

20 [00251] Results of the compressive strength, tensile properties, workability of the mixes and optical crack characterization are discussed below.

[00252] Example 4D: Results and discussion for mechanical properties and compressive strength under Example 4A

25 [00253] The summary of the mechanical properties of the specimens with different proportion of sand, tested after 28 days of curing are shown in FIG. 36 and 37.

[00254] Compressive strength - The results show that the unconfined compressive strength increases with increasing proportion of silica sand added. This means that the inclusion of sand strengthens the mechanical properties of the samples, allowing it to withstand higher structural load. On the other hand, the unconfined compressive
30 strength of the MSH-RS specimens remains relatively constant at about 75 MPa as proportion of sand increases, except for MSH-RS-2X. This coincides with experimental research where it was found that the compressive strength for ECC with river sand is

not significantly influenced by sand-binder ratio. This trend is contrary to the increasing trend seen in MSH-SS specimens. This may be due to their differences in matrix bonding. Moreover, MSH-00 has the highest compressive strength (88.70 MPa) as compared to other MSH-RS specimens which suggests that the addition of river sand do not improve the strength and hence may not be an optimum aggregate to use.

[00255] For the same sand/binder ratio, MSH-SS has a higher compressive strength than MSH-RS by about 10 to 15 MPa. This contracts with previous data whereby it was found that ECC with silica sand and river sand has comparable compressive strength. This may be due to the better fiber dispersion of the mix.

10 [00256] MSH-SS samples have an unconfined compressive strength of about 87 to 100 MPa while MSH-RS samples have an unconfined compressive strength of about 75 MPa, which is within the range of ECC (25 to 90 MPa). Nevertheless, they are still suitable for many structural applications.

15 [00257] **Example 4E: Results and discussion for tensile properties under Example 4A**

[00258] The tensile stress-strain curves of MSH-SS and MSH-RS specimens (based on best three specimens) are shown in FIG. 39 and 40, respectively.

20 [00259] All the specimens displayed strain-hardening behaviour with multiple cracks observed. Initial cracking strength is defined as the tensile stress detected on the formation of the first crack, interpreted from the stress measured at the end of the linear elastic region of the curve. This corresponds to the first drop observed in the stress-strain curve. Ultimate tensile stress and tensile strain capacity of the samples are defined as the tensile stress and strain right before the ultimate failure, as interpreted from the peak tensile stress and corresponding strain. These properties affect the tension test.

25 [00260] As the strain increases, tensile stress increases during the elastic stage. The progressive increase in load can result in the formation of the first crack which means the strain-hardening stage has occurred. At this stage, the specimen undergoes strain hardening behaviour, whereby tensile stress increases gradually with strain. This behaviour is also depicted by multiple small cracks which suggests its durability. The fiber bridging worsens nearing the strain-hardening portion of the curve. This coupled with localisation damage due to increased load contributes to the large drop in tensile

30

stress. The specimen also undergoes shrinkage of cracks as a result of spring effect of fiber-bridging when the load was released instantly after failure occurred.

[00261] It is evident that all the samples exhibit strain-hardening behaviours with multiple cracking. The tensile strain capacity for MSH-00 reaches 14.26%. When
5 11.11% sand is added, the tensile strain capacity reduces to 7.46% and 8.55% for MSH-SS-X and MSH-RS-X respectively. The tensile strain capacity is further increased to 9.29% and 9.07% for MSH-SS-2X and MSH-RS-2X when a sand content of 20% is added. The strain capacity is then further reduced to 5.42% and 6.85% for MSH-SS-3X and MSH-RS-4X respectively at 33.33% sand and 3.13% and 2.56% for MSH-SS-4X
10 and MSH-RS-4X respectively at 40% sand. In addition, the initial cracking strength of MSH-SS and MSH-RS specimens generally increase with sand content. Thus, MSH-SS and MSH-RS specimens revealed consistent results with each other.

[00262] When the silica sand content increases, the width of the cracks are increased. These can be depicted by the long drops in the stress-strain-curves, indicating larger
15 sized cracks. On the other hand, when river sand content increases, the drops in the stress-strain-curve for MSH-RS specimens are shorter as compared to the drops in the stress-strain-curved for MSH-SS specimens. This suggests that river sand samples have smaller crack width than silica sand samples which is supported by crack characterisation trends (FIG. 41 and 42).

[00263] When sand/binder ratio increases from 0 to 0.667, the initial cracking strength for MSH-SS and MSH- RS samples generally increase from 0.74 MPa to 3.27 MPa and 0.74 MPa to 1.01 MPa respectively. This may be attributed to the minimising of internal cracks formed on the specimens before demoulding since the increased proportion of sand helps to reduce shrinkage. Moreover, as proportion of sand increases, matrix
25 toughness increases. This is due to more aggregates debonding and deflecting cracks around the interfacial zone since there is an increase in surface abrasion. Thus, this results in an increase in tortuosity of crack propagation path and higher energy required for crack propagation and thus matrix toughness increases.

[00264] For the same sand to binder ratio, MSH-SS specimens have a higher initial
30 cracking strength than that of MSH-RS specimens. This is unexpected as it contradicts with previous research which states that in general, an increase in aggregate size results in an increase in first cracking strength.

[00265] FIG. 43 shows the relationship between ultimate tensile strength and sand/binder ratio for MSH specimens. From FIG. 43, the ultimate tensile strength generally increases from 2.46 to 4.53 MPa with increasing amount of silica sand but generally decreases from 2.46 to 1.49 MPa with increasing amount of river sand. This is consistent with previous research where it reported that there was an increase in ultimate tensile strength when proportion of silica sand increases.

[00266] However, when only comparing the sand/binder ratio from 0 to 0.25, it is observed that the ultimate strength increases for both MSH-SS and MSH-RS specimens which suggest that a sand/binder ratio of 0.125 and 0.25 are optimal. On the other hand, when the sand/binder ratio increases from 0.25 to 0.667, the ultimate tensile strength for MSH-RS specimens decreases from 2.93 to 1.49 MPa but increases from 3.85 to 4.53 MPa for MSH-SS specimens. Thus, it suggests that a sand/binder ratio of more than 0.5 may not recommended unless for certain applications that allows such ratio of more than 0.5.

[00267] Given that for ECC, the ultimate tensile strength may be dependent on the minimum fiber bridging ability when multiple cracks are formed, fiber dispersion is one of the main factors in influencing it. This may mean that there is good fiber-bridging for MSH-SS specimens but not for MSH-RS specimens after a sand/binder ratio of 0.25 is reached. This may be due to increased interlocking and friction between river sand compared to silica sand due to its larger particle size when sand/binder ratio increases. This may thus lead to a decrease in workability, resulting in poorer homogenous mix and disruption to fiber-bridging. It may also be due to the larger decrease in the percentage of cement paste, in terms of volume, per unit MSH-RS specimens as compared to MSH-SS specimens which might affect the fiber-bridging ability.

[00268] In addition, the ultimate tensile strength of MSH-RS specimens is always lower than that of MSH-SS specimens for the same proportion of sand added. Thus, since river sand are larger and coarser than silica sand, there may be poorer uniform fiber dispersion which may weaken the interfacial bonding between the fiber and matrix, resulting in lower ultimate tensile strength.

[00269] FIG. 44 shows the relationship between tensile strain capacity and sand/binder ratio for MSH specimens. For both MSH-SS and MSH-RS specimens, tensile strain capacity decreases with increasing amount of sand added. When the amount of sand

increases, there is higher interfacial frictional stress which result in fiber surface abrasion being more severe. This may thus lead to increased fiber breakage due to poor fiber bridging properties, reducing the ability to sustain multiple cracks.

[00270] Nevertheless, for all batches, strain-hardening behaviour with multiple
5 cracking can be observed as shown in FIG. 39 and 40. MSH-SS-3X, MSH-SS-4X, MSH-RS-3X have attained desirable tensile strain capacity, using a reference of tensile strain capacity of a range 3% to 7%. On the other hand, MSH-SS-X, MSH-SS-2X and MSH-RS-X and MSH-RS-2X have obtained ultra-high strain capacity of more than 7%. This suggests the possibility of using sand in MSH mixes to reduce cost while attaining
10 desirable strain-hardening behaviour. Given that the tensile strain capacity of MSH-RS-2X and MSH-SS-2X have the highest tensile strain of about 9%, a sand/binder ratio of 0.25 is advantageous.

[00271] Generally, at a given sand/binder ratio, MSH-SS specimens have a higher tensile strain capacity of about 1% more than MSH-RS samples. This may be due to
15 silica sand being rounder and smaller in size which reduces friction at the interfacial zone, improving the fiber distribution in the mix.

[00272] Nevertheless, their tensile strain capacity for the same sand/binder ration are still comparable. One reason for this possibility is that there is sufficient bridging stress within the matrix-fiber interface. This also suggests that the size of aggregates do not
20 have significant impact on tensile properties and thus, they are suitable alternatives to be used to reduce the cost of ECC while obtaining a desirable tensile strain capacity.

[00273] Example 4F: Results and discussion for fiber failure under Example 4A

[00274] To examine the type of fiber failure, the specimen was pulled apart using the uniaxial tension machine after failing in tension. Figure 19 show the type of failure
25 mode (fiber pull-out) for MSH-SS and MSH-RS specimens.

[00275] The type of fiber failure is dependent on the tensile strength of fiber and the bonding between the fiber and matrix. As PE fibers are hydrophobic in nature, there may be weaker bonding between the fiber and matrix which result in weaker bridging effect. This thus result in a fiber pull-out failure mode as the matrix is not be able to
30 hold the fiber in place at the failure surface. As such, a specimen failing by fiber pull-out method suggest that the fibers have strong bonding and bridging actions. Fiber pull-out failure mode is thus advantageous to the tensile performance of ECC.

[00276] Example 4G: Results and discussion for crack characterization under Example 4A

[00277] A summary of the crack characterization of MSH-SS and MSH-RS specimens are shown in FIG. 41 and 42, respectively. The crack patterns of MSH-SS and MSH-RS specimens can be seen in FIG. 46 and 47, respectively.

[00278] FIG. 46 and 47 show the crack patterns of MSH-SS and MSH-RS specimens, respectively. It is evident that all the specimens except for MSH-RS-3X and MSH-RS-4X have uniformly distributed and saturated cracks.

[00279] From FIG. 41, it can be observed that MSH-00 have an average crack width of 125.6 μm which is higher than expected. This may be due to the ultra-high tensile strain capacity (14.26%) attained. As sand/binder ratio increases from 0 to 0.125, average number of cracks decreases from 262 to 231, average crack width decreases from 125.6 to 91.3 μm while average crack spacing increases slightly from 1.49 to 1.61 mm. This can be attributed to the lower tensile strain observed, from 14.26% to 7.46%, with lesser multiple cracking seen. As sand/binder content increases from 0.125 to 0.25, the specimens have similar number of crack count, average crack width and crack spacing which suggests that the increase in sand content do not significantly affect the crack characteristics, as seen in the crack patterns of MSH-SS-X and MSH-SS-2X (FIG. 46).

[00280] When the sand/binder content is doubled (0.25 to 0.50), average number of cracks decreases by half (from 242 to 128) and crack spacing is doubled (from 1.61 to 3.28 mm). This coincides with the tensile properties of MSH-SS-2X and MSH-SS-3X since MSH-SS-2X has a tensile strain capacity of about two times higher than MSH-SS-3X. The increase in sand/binder ratio from 0.5 to 0.67 result in a decrease in average number of cracks by about 3 times from 128 to 35 and increase in crack spacing by four times from 3.28 to 12.0 mm, respectively.

[00281] From FIG. 42, as sand/binder ratio increases from 0 to 0.125, average number of cracks and cracks spacing are relatively constant while average crack width decreases. Likewise, for a sand/binder ratio of 0.125 to 0.25, the average number of cracks and average crack width for MSH-RS specimens are constant, which is consistent with MSH-SS specimens. This can be attributed to them having relatively similar tensile strain capacity. As sand/binder ratio increases from 0.25 to 0.5, MSH-

RS specimens have less cracks and larger average crack spacing which is in line with poorer tensile strain capacity. As sand/binder ratio increases from 0.5 to 0.667, average crack spacing increases by about half while the number of cracks decreases by about half which is evident from FIG. 47. This coincides with the decrease in tensile strain capacity by about half (from 6.85% to 2.56%).

[00282] In general, for both MSH-RS and MSH-SS specimens, the average number of cracks decreases while the average crack spacing increases (FIG. 49) as sand/binder ratio increases. This is expected as tensile strain capacity decreases as amount of sand increases. From FIG. 48 and 49, the average crack width and crack spacing for a sand/binder ratio of 0.125 and 0.25 are similar. This is expected as MSH-RS-X and MSH-SS-X have a similar tensile strain capacity of about 8% while MSH-RS-2X and MSH-SS-2X have a similar tensile strain capacity of 9%. In general, as sand/binder ratio increases, tensile strain capacity decreases and average crack width increases. However, MSH-RS-4X has a low tensile strain capacity of 2.56% and small average crack width of about 50 μm , which is unexpected. This may be due to micro cracks forming near the failure surface as seen in FIG. 47.

[00283] For the same sand/binder ratio, MSH-RS specimens have more cracks count than MSH-SS specimens, despite having a lower tensile strain capacity. The use of a larger aggregate size may introduce flaw sites, thus resulting in increase in average number of cracks.

[00284] Moreover, MSH-RS specimens have an average crack width of less than 100 μm regardless of the sand/binder ratio, which suggests that the increase in river sand content do not have significant influence on the crack width. Moreover, for specimens to undergo self-healing process, a crack width of less than 100 μm is preferably required. Thus, this indicates that MSH-RS specimens have high ductility. On the other hand, for MSH-SS specimens, as sand/binder ratio increases, crack width increases which suggest that the amount of silica sand affects the crack width. Thus, since MSH-SS-X and MSH-SS-2X have crack width of about 90 μm , the desirable sand/binder content may be 0.125 and 0.25.

[00285] **Example 4H: Results and discussion for workability under Example 4A**

[00286] A summary of the workability of MSH-SS and MSH-RS mixes are shown in Table 6.

[00287] Table 6 – Flow table values

Mix	Diameters measured (cm)				Average Diameter (cm)	Average Diameter (cm)	STDEV
	D1	D2	D3	D4			
MSH-SS-4X-1	16.9	15.3	16.6	16.5	16.33	17.4	1.50
MSH-SS-4X-2	18.7	19	17.9	18.2	18.45		
MSH-RS-X-1	16.1	15.3	15.1	14.5	15.25	14.74	0.72
MSH-RS-X-2	14	13.9	14.5	14.5	14.23		
MSH-RS-3X-1	16	15.6	16	16.5	16.03	16.45	0.6
MSH-RS-3X-2	16.8	17	17	16.7	16.88		
MSH-RS-4X-1	15.1	14.8	15.5	15.5	15.23	15.23	

[00288] From Table 6, for MSH-RS specimens, as proportion of sand increases, average diameter increases from 14.74 to 16.45 as sand/binder ratio increases from 0.125 to 0.5. However, average diameter decreases as sand/binder ratio increases from 0.5 to 0.6 which is expected. This is due to the aggregates having a larger surface area, absorbing more water resulting in a decrease in the workability.

[00289] Example 4I: Summary of under Example 4A

[00290] Examples 4A to 4H investigated the feasibility and effectiveness of using MSH cementitious system as an alternative to PC due to rising environmental concerns. The mechanical performance of MSH-ECC samples incorporating different types and proportion of sand after 28 days of curing were examined with the main objective of evaluating the possibility of adding sand into the mix to reduce cost while achieving desirable strain-hardening properties.

[00291] Both MSH-RS and MSH-SS specimens have shown strain-hardening behaviour with multiple cracking after uniaxial tensile testing. Both specimens have comparable strain-hardening capacity which suggests that the type of aggregate do not have significant effect on strain-hardening capacity.

[00292] As sand/binder ratio increases from 0 to 0.667, ultimate tensile strength increases from 2.46 to 4.53 MPa for specimens with silica sand. On the other hand, ultimate tensile strength increases from 2.46 to 2.93 MPa as sand/binder ratio increases to 0.25 but decreases from 2.93 to 1.49 MPa when sand/binder ratio is further increased to 0.667 due to poor fiber bridging. This suggests that a sand/binder ratio of less than

0.25 is optimal. Moreover, the tensile strain capacity (about 8% to 9%), average crack width, average crack spacing, and number of cracks are comparable for a sand/binder ratio of 0.125 and 0.25, which suggests that these two batches are optimal. Nevertheless, other batches of river sand and silica sand are also able to obtain a tensile strain-capacity of at least 3%, except for MSH-RS-4X (sand/binder ratio of 0.667).

[00293] MSH-SS specimens have increasing compressive strength with increasing sand content, unlike MSH-RS specimens which have a relatively constant compressive strength (of about 75 MPa). Both specimens have increasing initial cracking strength as sand content increases due to increase in matrix toughness. Even though, MSH-SS specimens had better mechanical properties than MSH-RS specimens, MSH-RS specimens still have relatively good engineering properties of ECC, thus suggesting that the use of river sand is a possibility in reducing the cost of ECC while achieving strain-hardening behaviour.

[00294] To summarise, MSH cementitious system with the inclusion of sand can be used as an alternative to PC since it is able to obtain desirable mechanical properties and be cost efficient.

[00295] Example 5: Commercial and Potential Applications

[00296] One of the commercial applications of the present composite and pre-mix lies in the manufacturing of unreinforced structural and building components, which include bricks, blocks and pavers. It should be noted that the present SHMSHC applications are not limited to non-structural applications. SHMSHC has the potential to be used in precast and site-cast structural applications wherever the tensile and compressive strength requirements are met.

[00297] While the present disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the present disclosure as defined by the appended claims. The scope of the present disclosure is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A strain hardening cement pre-mix comprising:
a reactive magnesium oxide cement;
an amorphous silica source; and
a fiber.
2. The strain hardening cement pre-mix of claim 1, wherein the amorphous silica source comprises microsilica, rice husk ash, or waste glass.
3. The strain hardening cement pre-mix of claim 1 or 2, wherein the fiber comprises a polymeric fiber, a metallic fiber, or a naturally-occurring fiber.
4. The strain hardening cement pre-mix of any one of claims 1 to 3, wherein the fiber is present in an amount of 15 vol% or less.
5. The strain hardening cement pre-mix of any one of claims 1 to 4, wherein the fiber is coated with an oiling agent or carbon nanofiber.
6. The strain hardening cement pre-mix of any one of claims 1 to 5, wherein the fiber has a diameter ranging from 10 μm to 100 μm .
7. The strain hardening cement pre-mix of any one of claims 1 to 6, wherein the fiber has a length ranging from 5 mm to 30 mm.
8. The strain hardening cement pre-mix of any one of claims 1 to 7, wherein
 - (i) the reactive magnesium oxide cement is present in an amount of 30 wt% to 70 wt% based on the reactive magnesium oxide cement and the amorphous silica source, and/or
 - (ii) the amorphous silica source is present in an amount of 30 wt% to 70 wt% based on the reactive magnesium oxide cement and the amorphous silica source.

9. The strain hardening cement pre-mix of any one of claims 1 to 8, further comprising a water reducing agent, a viscosity controlling agent, and/or an aggregate.
10. A strain hardening magnesium-silicate-hydrate composite formable from the strain hardening cement pre-mix of any one of claims 1 to 9, comprising:
 - magnesium-silicate-hydrate; and
 - a fiber dispersed therein.
11. The strain hardening magnesium-silicate-hydrate composite of claim 10, wherein the fiber comprises a polymeric fiber, a metallic fiber, or a naturally-occurring fiber.
12. The strain hardening magnesium-silicate-hydrate composite of claim 10 or 11, wherein the fiber is present in an amount of 15 vol% or less.
13. The strain hardening magnesium-silicate-hydrate composite of any one of claims 10 to 12, wherein the fiber is coated with an oiling agent or carbon nanofiber.
14. The strain hardening magnesium-silicate-hydrate composite of any one of claims 10 to 13, wherein the fiber has a diameter ranging from 10 μm to 100 μm .
15. The strain hardening magnesium-silicate-hydrate composite of any one of claims 10 to 14, wherein the fiber has a length ranging from 5 mm to 30 mm.
16. The strain hardening magnesium-silicate-hydrate composite of any one of claims 10 to 15, further comprising a water reducing agent, a viscosity controlling agent, and/or an aggregate.
17. A method of forming the strain hardening cement pre-mix of any one of claims 1 to 9, the method comprising:
 - mixing an amorphous silica source with a reactive magnesium oxide cement to form a dry mixture; and

dispersing a fiber in the dry mixture.

18. The method of claim 17, further comprising mixing the dry mixture with a water reducing agent, a viscosity controlling agent, and/or an aggregate.

19. A method of forming the strain hardening magnesium-silicate-hydrate composite of any one of claims 10 to 16, the method comprising:

mixing a reactive magnesium oxide cement with water;

mixing an amorphous silica source to the reactive magnesium oxide cement and the water to form a mixture;

dispersing a fiber in the mixture; and

curing the mixture comprising the fiber to form the strain hardening magnesium-silicate-hydrate composite.

20. The method of claim 19, further comprising mixing the water with a water reducing agent and/or a viscosity controlling agent prior to mixing the reactive magnesium oxide cement with the water.

21. The method of claim 19 or 20, wherein curing the mixture comprises curing the mixture for at least 28 days at a relative humidity of at least 60% and at a temperature more than 0°C and less than 60°C.