Summary

The present disclosure provides a method of preparing a hydrogel, comprising:

(i) preparing a mixture of water-soluble polymer, inorganic acid, and radiation-reflecting inorganic particles;

(ii) adding a crosslinking agent to the mixture to form a hydrogel precursor;

(iii) freezing and thawing the hydrogel precursor thereby forming a hydrogel,

wherein the hydrogel precursor comprises:

about 5 wt% to about 30 wt% of water-soluble polymer;

about 0.3 wt% to about 2.5 wt% of inorganic acid;

about 0.05 wt% to about 0.5 wt% of crosslinking agent; and

about 3 wt% to about 70 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor.

According to one aspect, the present disclosure provides a method of preparing a hydrogel, comprising:

(i) preparing a mixture of water-soluble polymer, inorganic acid, and radiation-reflecting inorganic particles;

(ii) adding a crosslinking agent to the mixture to form a hydrogel precursor;

(iii) freezing and thawing the hydrogel precursor thereby forming a hydrogel,

wherein the hydrogel precursor comprises:

5 wt% to 30 wt% of water-soluble polymer;

0.3 wt% to 2.5 wt% of inorganic acid;

0.05 wt% to 0.5 wt% of crosslinking agent; and

3 wt% to 67 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor, and

wherein the radiation-reflecting inorganic particle is barium sulfate.

Advantageously, the method of preparing the hydrogel is a simple, scalable and cost-effective manufacturing process for mass production. The method disclosed is simple and easy to perform which can be conducted easily in manufacturing facilities and laboratories.

The method of adding a crosslinking agent to the mixture to form a hydrogel precursor may produce chemical crosslinks in the hydrogel. The method of freezing and thawing the hydrogel precursor may produce physical crosslinks in the hydrogel. This advantage produces a hydrogel with multi-crosslinks, which comprises a hydrogel with both physical and chemical crosslinks. Advantageously, with both physical and chemical crosslinks in the hydrogel, this may provide a better and more stable hydrogel with longer lifetime and better structural integrity of the hydrogel.

The present disclosure also provide a hydrogel precursor for forming a hydrogel comprising:

about 5 wt% to about 30 wt% of water-soluble polymer;

about 0.3 wt% to about 2.5 wt% of inorganic acid;

about 0.05 wt% to about 0.5 wt% of crosslinking agent; and

about 3 wt% to about 70 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor.

Advantageously, the hydrogel precursor comprises water-soluble polymer, inorganic acid, crosslinking agent and radiation-reflecting inorganic particle which may be purchased or obtained easily. Also advantageously, the hydrogel precursor may be easily combined, mixed,

incorporated or integrated with other materials in order to further enhance the hydrogel's stability and mechanical properties.

According to yet another aspect, there is provided a hydrogel obtained by the method as disclosed herein.

The present disclosure also provides a hydrogel prepared by freeze-thawing the hydrogel precursor as disclosed herein.

According to another aspect, the present disclosure provides a hydrogel prepared by freeze-thawing a hydrogel precursor, wherein the hydrogel precursor comprises:

5 wt% to 30 wt% of water-soluble polymer;

0.3 wt% to 2.5 wt% of inorganic acid;

0.05 wt% to 0.5 wt% of crosslinking agent; and

3 wt% to 67 wt% of a radiation-reflecting inorganic particle,

or

5 wt% to 25 wt% of water-soluble polymer;

0.3 wt% to 1.2 wt% of inorganic acid;

0.05 wt% to 0.25 wt% of crosslinking agent; and

30 wt% to 67 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor, and

wherein the radiation-reflecting inorganic particle is barium sulfate.

The present disclosure also provides a hydrogel comprising:

about 5 wt% to about 30 wt% of water-soluble polymer;

about 0.1 wt% to about 1.5 wt% of crosslinking agent; and

about 3 wt% to about 70 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel.

Advantageously, the hydrogel may comprise chemical and physical crosslinks. With both physical and chemical crosslinks, the hydrogel exhibits improved stability and mechanical strength. With the improved stability and mechanical strength, this results in a hydrogel with a longer lifetime which translates to cost-efficiency and cost-effectiveness in the long run.

Also advantageously, the hydrogel may be able to act as a cooler. The hydrogel may be able to utilize both evaporative and radiative cooling techniques to cooperatively achieve passive

cooling. This allows the hydrogel to cool high temperatures, for example in harsh tropical weather conditions. The combination of evaporative cooling and radiative cooling in the hydrogel may lead to unprecedented sub-ambient cooling performance even in weather conditions that are unfavored for conventional passive cooling technologies. The hydrogel may provide an efficient heat isolation layer through high radiation reflection and low thermal conductivity which enables cooling.

Further advantageously, the hydrogel may be combined, mixed, incorporated or integrated with other materials in order to further enhance its stability and mechanical properties. Furthermore, the hydrogel is easy to apply and may be used in various applications, materials and surfaces for cooling.

One such application of the hydrogel includes a use of hydrogel on buildings for cooling. The hydrogel may be applied on the walls and/or roofs of a building. Typically, cooling performance and efficiency of radiative cooling is dependent on the radiation exposure and it may be weakened on sidewalls of a building due to insufficient radiation through atmospheric window and radiation exposure arising from the tilted angle from a building. However, with the combination of both evaporative and radiative cooling in the hydrogel of the present invention, the hydrogel further advantageously offers and provides cooling even on sidewalls or blocked surfaces. The hydrogel may thus transfer heat better and enable better cooling performance and efficiency on all available sides of a building or and object applied/coated with the hydrogel. Also advantageously, the hydrogel with low solar reflectance (in turn reduces the dazzling effect under intensive sunlight), along with

with parasitic heat transfer (1) and water evaporation (2); and (b) shows the hydrogel with solar energy input (4) with parasitic heat transfer (1) and enhanced water evaporation (3).

Figure 7a

[Figure 7a] is a graph showing a comparison of water content and bound water ratio within Pure-Gel and Metagel-2.

Figure 7b

[Figure 7b] is a graph showing a storage and loss modulus of Pure-Gel and Metagel-2.

Figure 7c

[Figure 7c] is a graph showing a Differential Scanning Calorimeter (DSC) thermogram of water evaporation (a graph of heat flow (W/g) against temperature (°C)) within Pure-Gel and Metagel-2, with insets of schematic structures.

Figure 7d

[Figure 7d] is a graph (of intensity against wavenumber) showing Raman OH stretching mode of Pure-Gel and Metagel-2, where FW indicates free water and IW indicates intermediate water.

Figure 7e

[Figure 7e] is a graph showing a comparison on cooling performance (ACD and cooling cycle duration) with controlled water quantity exhibited by a water layer and a 10-mm-thick Metagel-2.

Figure 7f

[Figure 7f] is a graph showing an indoor evaporative cooling comparison and temperature rising comparison (under solar illumination) between Pure-Gel and Metagel-2, measured at a relative humidity of 60% ± 3% and solar intensity of 1000 W/m^2.

Figure 7g

[Figure 7g] is a graph showing a theoretical ACD of Metagel-2 at different thicknesses based on average tropical climate with reference to bare concrete (black dotted line) and state-of-the-art passive radiative cooler (PRC; grey line) with R_{solar}~ 98%, E_{LWIR}~ 98%, and thickness~ 500 μm.

Figure 7h

[Figure 7h] is a graph showing a thickness-dependent reciprocal ACD and cooling efficiency of Metagel-2 at different thicknesses.

Figure 7i

[Figure 7i] is a graph showing a solar intensity dependent output power density by evaporative (P_{evp}) and radiative (P_{rad}) cooling, and net output power density (P_{net}) of Metagel-2.

Figure 8

[Figure 8] is an optical image (photograph) showing the comparison of (1) hydrogel which is crosslinked with sulfuric acid, and (2) hydrogel which is crosslinked without sulfuric acid, after an hour (one hour) of adding crosslinking agent. Apart from the use of sulfuric acid, the same components are used. The (1) hydrogel which is crosslinked with sulfuric acid, is crosslinked within five minutes.

Figure 9

[Figure 9] (a) is an optical photograph showing the setup for precise recording, where solar shields are applied to prevent total diffused sunlight, and a pyrgeometer is used to record downwelling atmospheric radiation (DLR); and (b) is a graph showing the monitored rooftop radiations (solar and NIR-LWIR range) during a typical sunny day in Nanyang Technological University, Singapore.

Figure 10a

[Figure 10a] is a graph of concentration of NIH 3T3 fibroblast cells against cultivation time, showing the bio-compatibility test of a control and Metagel-2.

Figure 10b

[Figure 10b] is an optical image of Metagel-2 in accordance with the present invention with a dimension (18 cm x 9 cm x 2 mm) used in skin cooling test.

Figure 10c

[Figure 10c] is an optical image showing configuration of Metagel-2 (2mm) that is tightly attached on skin (same configuration in Figure 19f).

Figure 10d

[Figure 10d] is an IR image of Metagel-2 covered skin under indoor conditions where the IR images in Figure 10d and Figure 19f are all taken after a 20-minute stabilization.

Figure 11a

[Figure 11a] is a graph showing a 300-1300 nm reflectance of a hydrogel with increasing content of $BaSO_4$ particles (Pure-Gel; Metagel-1; Metagel-2; and Metagel-4).

Figure 11b

[Figure 11b] is a graph showing solar reflectance (solid line, left y-axis) and transmittance (dotted line, right y-axis) of Metagel-2 with different thicknesses.

Figure 11c

[Figure 11c] is a bar chart showing solar reflectance (grey) and transmittance (black) of Metagel-2 with different thicknesses.

Figure 12

[Figure 12] is a graph showing an attenuated total reflection (ATR) - Fourier-Transform Infrared (FTIR) spectrum of Pure-Gel and water-free Metagel-2, where left panel represents OH stretching mode and right panel represents OH bending mode. The peak positions and shift directions are labelled.

Figure 13a

[Figure 13a] is a bar chart showing the specific heat flow from a low temperature of -30 ℃ to 30 ℃ (left y-axis) and water mass (right y-axis) of different hydrogels from the measurements of Differential Scanning Calorimetry (DSC).

Figure 13b

[Figure 13b] is a graph showing the calculated bound water content (%) within different hydrogels.

Figure 14

[Figure 14] is a bar graph showing the thermal conductivity of Metagel-2 under different wet and dry states. The range of thermal conductivity of pure PVA hydrogel in dry state is shaded (▨) as shown in the figure for comparison.

Figure 15

[Figure 15] shows heat transfer models for theoretical analysis; where (a) shows a heat transfer model based on experimental setup in field test for validating the simulation accuracy, where side evaporation is also considered; and (b) shows a periodic heat transfer model when considering a large enough surface area, where side evaporation is neglected. A human comfortable indoor temperature (T_{in} = 25 ℃) is maintained for evaluation of active cooling demand with different surface covers. All data presented in this work are based on periodic model.

Figure 16

[Figure 16] shows a Raman spectrum (upper panel, where FW indicates free water and IW indicates intermediate water) and related IW/FW ratio (lower panel) within different hydrogels (Pure-Gel; Metagel-2; and Metagel-4).

Figure 17a

[Figure 17a] is a graph (upper) showing the recorded temperature of cooled aluminium (Al) substrate using two cooling systems (one using a bare aluminium with conventional spray cooling, and the other using Metagel-2), where atmospheric conditions, including ambient temperature, solar intensity and RH are recorded in the lower graph for reference.

Figure 17b

[Figure 17b] is an optical image (left) and schematic (left) of setup for comparison between hydrogel and conventional evaporative cooling by spraying water.

Figure 18a

[Figure 18a] is a schematic illustration of the setup for indoor evaporating cooling test.

Figure 18b

[Figure 18b] is a graph showing the temperature recording during indoor evaporative cooling test of Pure-Gel (4mm).

Figure 18c

[Figure 18c] is a graph showing the temperature recording during indoor evaporative cooling test of Metagel-2 (4mm), where the introduction of solar illumination (1000 W/m^2) proves the effectiveness of sub-ambient passive cooling in Metagel-2.

Figure 19a

[Figure 19a] is a graph showing a recorded temperature profile of 24-h indoor passive cooling where the inset illustrates an IR image of Metagel-2.

Figure 19b

[Figure 19b] is a graph showing an outdoor cooling performance of Metagel-2 at daytime of a typical sunny day, where atmospheric conditions, including ambient temperature (upper graph), solar intensity and RH (in lower graph) are recorded for reference.

Figure 19c

[Figure 19c] is a graph showing an outdoor cooling performance of Metagel-2 at night-time of a typical day, where atmospheric conditions, including ambient temperature (upper graph), solar intensity and RH (in lower graph) are recorded for reference.

Figure 19d

[Figure 19d] is a graph showing a metagel-2 sidewall (outdoor) cooling performance compared with the state-of-the-art passive radiative cooler PRC (radiative cooler side wall; and radiative cooler rooftop), where atmospheric conditions, including ambient temperature (upper graph), solar intensity and RH (in lower graph) are recorded for reference.

Figure 19e

[Figure 19e] is a graph showing an outdoor sub-ambient cooling achieved by coloured Metagel-2 (green, red and yellow); where atmospheric conditions, including ambient temperature, solar intensity, RH, and downwelling radiation (DLR), are recorded for reference.

Figure 19f

[Figure 19f] is an IR image showing outdoor sub-ambient cooling on human skin (the same Metagel-2 sample as that in Figure 10c), measured at an air temperature of 33°C, a relative humidity of 60% and solar intensity of 1000 W/m^2 (≈ 1 Sun). IR images of Figure 10d and Figure 19f are all taken after a 20-minute stabilization.

Figure 20a

[Figure 20a] is a graph showing the optical properties, i.e., solar reflectance (left y-axis) and LWIR emissivity (right y-axis) of Metagel-2 and the best reported radiative cooler used for sidewall cooling (e.g. Radiative Cooler Rooftop and Radiative Cooler Sidewall).

Figure 20b

[Figure 20b] is a graph showing the visible reflectance spectrum of controlled hydrogels with different $BaSO_4$ content (Metagel-0.1; Metagel-0.5; and Metagel-1), where the inset shows the optical images of corresponding hydrogels under sunlight.

Figure 20c

[Figure 20c] is a graph showing the visible reflectance spectrum of a typical commercial solar reflective construction paint (NIPPON SOLAREFLECT Si).

Figure 21

[Figure 21] is an optical photograph showing the fire safety and retardant performance evaluation of Metagel-2 under direct burning at different directions (horizontal and vertical), where the applied Metagel-2 has a thickness of 4 mm.

Figure 22

[Figure 22] shows several optical images (photographs) demonstrating the mechanical properties (brittleness, flexibility, elasticity and puncture-ability) of (A) free-standing chemical crosslinked metagel, (B) free-standing physical crosslinked metagel and (C) fabric-supported multi-crosslinked metagel (comprising both physical and chemical crosslinks).

Figure 23

[Figure 23] is a graph showing the tensile test results (Force (N) against Elongation (mm)) of a hydrogel with different crosslinking method, where chemical crosslinked is conducted with glutaraldehyde as a crosslinking agent; physical crosslinked is conducted with freeze-thawing method; and fabric-supported multi-crosslinked is with both chemical crosslinking method (with glutaraldehyde as crosslinking agent) and freeze thawing method, and fabric skeleton.

Figure 24a

[Figure 24a] is a schematic illustration showing cooling mechanisms of an APC.

Figure 24b

[Figure 24b] is a schematic illustration showing the working principles, cooling processes and active cooling demand (ACD) maintaining at comfortable indoor temperature with bare (left) and hydrogel-covered (right) concretes.

Figure 24c

[Figure 24c] is a graph showing a simulated scattering efficiency (300-1300 nm) with varying sizes of barium sulfate particles (BSP).

Figure 24d

[Figure 24d] shows a structural illustration (upper) of Metagel-2 and scanning electron microscope (SEM) image (lower left, scale bar is 1 μm) of Metagel-2, and a graph of BSP size distribution (lower right) in Metagel-2.

Figure 24e

[Figure 24e] is a graph showing a solar reflectance (%) spectrum of Pure-Gel in wet state, Metagel-2 in wet state and Metagel-2 in dry state (shaded area indicates the reflectance difference between the dry and wet Metagel-2).

Figure 24f

[Figure 24f] is a graph showing a transmittance (%) spectrum of Pure-Gel in wet state, Metagel-2 in wet state, and Metagel-2 in dry state.

Figure 24g

[Figure 24g] is an optical image (a photograph, upper) and infrared (IR) image (lower) of Metagel-2 under sunlight taken after 30-minute stabilization where ambient temperature is about 33°C, solar irradiation is about 1045W/m^2, and relative humidity (RH) is at about 60%.

Figure 24h

[Figure 24h] is a graph showing a long-wave infrared (LWIR) emittance spectrum of Metagel-2 in wet (solid lines) and dry (dotted lines) states, where shaded area labels the atmospheric window.

Figure 25

[Figure 25] is an optical image showing a Scanning Electron Microscopic (SEM) image of Pure-Gel, showing the average pore size in Pure-Gel is much smaller than that in hydrogel.

Figure 26

[Figure 26] is a graph showing the heat flow of pure water and Metagel-2 from water evaporation.

Figure 27

[Figure 27] is a graph showing the simulated temperature difference on the top surface (solid lines) and on the interface (dotted lines) depending on various evaporation enthalpy at 1500, 2000, and 2500 J/g.

Figure 28

[Figure 28] is a graph showing the indoor test temperature recording of Metagel-2 at different thicknesses (4mm, 6mm and 8mm). All samples were prepared with a diameter of 10 cm (circular film) to minimize the influence of edge surface.

Figure 29

[Figure 29] is a bar graph showing the water content monitoring of Metagel-2 with various thicknesses where the bar graph (using the left y-axis) shows the water weight of the different types of Metagel-2 (saturated, shrinking and dried) at thickness of 2mm, 4mm and 6mm; and where the line graph (using the right y-axis) shows the water ratio at shrinkage point of Metagel-2 with various thicknesses of 2mm, 4mm and 6mm.

Examples

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Chemicals And Materials

Chemicals used in this invention includes polyvinyl alcohol (PVA) with molecular weight (MW) of about 89000 to 99000, glutaraldehyde (50% aqueous solution), barium sulfate ($BaSO_4$) powder (of an average size of about 350 nm), and sulfuric acid (95%) were all purchased from Sigma-Aldrich. All chemicals were used without further purification. Silicone oil from KOYA® was applied as a mould-release agent to prevent mechanical deformation during gelation. The dyes used for coloured hydrogel fabrication was food dyes from Starbrand®.

The hydrolyzation rate and molecular weight of water-soluble polymer (or polymeric matrix) act importantly, usually a 99% hydrolyzation with high molecular weight (molecular weight of more than (>) 15W) is favoured.

Example 1: Preparation of Hydrogels

Hydrogel Fabrication Procedure

PVA solution was prepared at 100 ℃ with stirring in a sealed beaker (to prevent water loss) until a total homogeneous solution appears. The prepared PVA solution was cooled down to room temperature for further use. PVA solution was mixed with sulfuric acid with stirring for 1 hour. Barium sulfate ($BaSO_4$) was added to the mixture. glutaraldehyde solution was slowly added and stirred for 30 seconds. During the entire process, stirring speed was controlled properly to avoid formation of bubbles. The sample (hydrogel precursor) was moved into a mould for 24-hour gelation.

The mould was put into a freezer for freezing or deep freezing at a temperature of between about -40 °C to about -20 °C for a duration from about six hours to twelve hours depending on the thickness of the hydrogel. Afterwards, a layer of normal temperature water was added into the mould for thawing. A water bath may also be used for thawing. The frozen mixture may be thawed at a temperature of about 20 °C to about 30 °C for a duration of about 0.5 hours to about 3.5 hours. The freezing and thawing process may be repeated multiple times. The freeze-thaw process produces physical crosslinks. The resulting product is a multi-crosslinked hydrogel containing both chemical and physical crosslinks. During the process of thawing the hydrogel in water or water bath, sulfuric acid is washed off and removed from the hydrogel.

To ensure exactly the same components were used, barium sulfate may be first dispersed in the H_2SO_4 solution before mixing with PVA solution.

Various types of moulds may be used, for example, plastic moulds, metal moulds, or polytetrafluoroethylene (PTFE) moulds. A release agent may be used in combination with the mould. For example, silicone oil may be used when using plastic.

The above method is compatible with continuous production, where skeleton materials (such as porous fabric or foam) can be composited with the hydrogel for further enhancement of mechanical modulus.

Through an integrated crosslinking process (to give physical and chemical cross linkings), a cost-effective, high-water content, mechanically stable and low swelling ratio hydrogel can be obtained. The method is highly distinct from traditional hydrogel fabrication where the main materials choice is strict due to integrated process.

Pure-Gel Fabrication Procedure

A comparative sample (Pure-Gel) was also prepared. Pure-Gel sample was prepared by mixing PVA solution with sulfuric acid with stirring for 1 hour. glutaraldehyde solution was slowly added and stirred for 30 seconds. The prepared Pure-Gel sample was further moved into a silicone oil coated polytetrafluoroethylene (PTFE) mould for 24-hour gelation.

The mould was put into a freezer for freezing or deep freezing at a temperature of between about -40 °C to about -20 °C for a duration from about six hours to twelve hours depending on the thickness of the hydrogel. Afterwards, a layer of normal temperature water was added into the mould for thawing. A water bath may also be used for thawing. The frozen mixture may be thawed at a temperature of about 20 °C to about 30 °C for a duration of about 0.5 hours to about 3.5 hours. The freezing and thawing process may be repeated multiple times. The freeze-thaw process produces physical crosslinks. The resulting product is a multi-crosslinked hydrogel containing both chemical and physical crosslinks.

Example 2: Hydrogels

Herein, the hydrogel is not a pure polymeric material since radiation-reflecting inorganic particles was added in the hydrogel to provide radiating-reflecting properties. The hydrogel samples were labelled a metagel, i.e., a metamaterial based on hydrogel. The names of the samples were labelled as “Metagel-x”, where x defines the critical parameters of the specific metagel sample. The hydrogel with pure polymeric components was named as “Pure-Gel”.

Example 2a: Hydrogel Precursor

Hydrogel precursors (precursor of Metagel-0.1, precursor of Metagel-0.5, precursor of Metagel-1, precursor of Metagel-2, precursor of Metagel-4) were prepared using the method in Example 1. The weight percentage of the hydrogel precursor components in Metagel-0.1, Metagel-0.5, Metagel-1, Metagel-2, Metagel-4, based on the total weight of hydrogel, is tabulated in Table 1a.

Hydrogel precursors were named/labelled according to the ratio of each component, particularly the barium sulfate ($BaSO_4$) component. For example, precursor of Metagel-2 indicates 2g of barium sulfate. Precursor of Metagel-4 indicates 4g of barium sulfate.

Hydrogels with different thicknesses were all prepared based on these component ratios.

Table 1a. *Weight % of components in hydrogel precursors, based on the total weight of hydrogel precursors.*

Hydrogel Precursors	PVA (wt%)	H_2SO_4 (wt%)	Glutaraldehyde (wt%)	$BaSO_4$ (wt%)	Total Water (wt%)	Total
Precursor of Metagel-0.1	~26 (25.5-26.5)	1-2	0.2-0.4	~4.7 (4.2-5.2)	~68 (67.5-68.5)	100 wt%
Precursor of Metagel-0.5	~18 (17.5-18.5)	1-2	0.2-0.4	~20 (19.5-20.5)	~60 (59.5-60.5)	100 wt%
Precursor of Metagel-1	~20 (19.5-20.5)	0.5-1	0.1-0.2	~33 (32.5-33.5)	~47 (46.5-47.5)	100 wt%
Precursor of Metagel-2	~15 (14.5-15.5)	0.5-1	0.1-0.2	~50 (49.5-50.5)	~35 (34.5-35.5)	100 wt%
Precursor of Metagel-4	~10 (9.5-10.5)	0.5-1	0.1-0.2	~66 (65.5-66.5)	~23 (22.5-23.5)	100 wt%

Example 2b: Hydrogel

Hydrogel (Metagel-0.1, Metagel-0.5, Metagel-1, Metagel-2, Metagel-4) were prepared using the method in Example 1 and the hydrogel precursors in Example 2a.

Hydrogels were named/labelled according to the ratio of each component in the hydrogel precursor, particularly the barium sulfate ($BaSO_4$) component. For example, Metagel-2 indicates 2g of barium sulfate in the precursor of Metagel-2. Metagel-4 indicates 4g of barium sulfate in the precursor of Metagel-4.

The structure and components of a hydrogel are illustrated in Figure 3, where the grey section ( ) represents free water, the circle ( ) represents a radiation-reflecting inorganic particle and the wavy lines ( ) represents a polymeric chain of a water-soluble polymer.

Example 3: Cooling Mechanisms

The hydrogel utilises both evaporative cooling and passive radiative cooling techniques for cooling. The hydrogel comprises an integrated structure which exhibits radiation-reflection (i.e. solar reflection), solar blocking, LWIR emission, and evaporation cooling functions (as shown in Figures 4 and 5).

The framework of the hydrogel is composed of crosslinked polymeric chains, with abundant porous structure. Embedded particles are homogeneously distributed in the polymeric matrix, stabilized by hydrogen bonds forming between particle surface and hydrated polymeric network. Free water occupies inner pore volume, acting as dynamic heat exchange medium through evaporation and transport behaviours. In the hydrogel, free water is stably confined by strong hydrogen bond interaction, leading to slow water loss. The uniform porous structure allows

Example 4: Characterization of Hydrogels

Instruments And Analytical Techniques for Hydrogel Characterizations

Scanning electron microscopic (SEM) images were obtained by a field-emission scanning electron microscopy (JEOL 7600). Infrared (IR) images were taken by a portable IR camera (FLIR E60). Solar range optical properties were characterized by a UV-vis-NIR spectrometer (PerkinElmer Lambda 950) coupled with an internal integrating sphere (150 mm InGaAs). Differential scanning calorimetry (DSC) test was conducted with two modes: water evaporation enthalpy test was conducted with DSC Q200 (TA Instrument), and water melting behaviour test was conducted with DSC Q10 (TA Instrument). Raman signal was collected by a Raman spectrometer (WITEC alpha 300 R confocal Raman system) with a customized sample stage. Before testing, the system was calibrated with Si peak at 520 cm^{-1} to keep the measurement consistent. IR emittance spectrum and attenuated total reflectance (ATR) test was obtained through recording IR reflectance spectrum by a Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum Frontiers) equipped with a gold integrating sphere (PerkinElmer Mid-IR Integrating Sphere, with 8-degree incident angle). The thermal conductivity was measured by a Hot Disk 2500S based on bulk type mode. Rheological properties were evaluated through a dynamic mechanical analysis system (DMA Q800, TA Instrument). The solar simulator for indoor illumination test was a Newport LCS-100 setup.

Sample Preparation for Hydrogel Characterizations

Dried hydrogels were used for optical measurement and characterization, where the hydrogel was treated with freeze drying method under -40 °C for two days, in which the porous structure was kept maintained for light scattering characterizations.

Dried hydrogels for thermal conductivity measurement were treated under high temperature (60 ℃) in an oven for 2 days to collapse the pores. By doing so, this minimizes the influence of air within pores on the measured thermal conductivity.

Sections below and Figure 7a to Figure 7i shows the results for hydrogel characterization.

Electrostatic Interaction Between Barium Sulfate Particles and Polymer Chain

As a radiation-reflecting inorganic particle or a radiation scattering agent, barium sulfate $BaSO_4$ nanoparticles should be stabilized in the porous polymer framework for long-term usage. ATR-FTIR test was conducted to reveal the interaction between $BaSO_4$ nanoparticles and polymer framework within dried hydrogel samples.

Figure 12 is a graph showing an ATR-FTIR spectrum of Pure-Gel and water-free Metagel-2, where left panel represents OH stretching mode and right panel represents OH bending mode.

According to Figure 12, it is observed that the electrostatic interaction between $BaSO_4$ and polymer chain restrains the vibration of hydroxyl group, leading to a red shift in stretching mode (left panel), and suggesting a stronger intermolecular interaction of hydrogen bonding. Meanwhile, the blue shift of bending mode of hydroxyl group reveals a restrained intramolecular

Dynamic Mechanical Analysis (DMA)

Through dynamic mechanical analysis, hydrogel rheological property can be characterized for evaluating compositional effect. Energy storage and dissipation features are expected for such viscoelastic material, which are mainly characterized by storage modulus and loss modulus, respectively. The storage modulus of hydrogel is larger than its loss modulus ascribing to the porous structure (Figure 7b). Upon the addition of $BaSO_4$ particles, these two moduli are greatly enhanced due to the strong electrostatic interaction enhancing the mechanical properties. Moreover, steric hinderance effect (SHE) is further verified by the increased loss modulus.

Thermal Conductivity

As depicted in Figure 14, the thermal conductivity of Metagel-2 decreases in dry state. Poor thermal conductivity is favoured for external cooling application due to excellent heat isolation that effectively prevent incoming atmospheric thermal energy.

Compared to the saturated pure PVA hydrogel (Pure-Gel), saturated Metagel-2 exhibits lower thermal conductivity, which is even slightly lower than pure water, indicating excellent heat isolation. Besides, both saturated and dried Metagel-2 exhibit lower thermal conductivity than those of pure PVA hydrogel (Pure-Gel). Intermolecular interactions by hydrogen bonding (bound water molecules on polymer chain) are proven to enhance the thermal conductivity of hydrated polymer. Interpenetrated $BaSO_4$ particles spatially (steric hindrance effect) minimizes the formation of hydrogen bonding interactions between separate polymer chains, further lowering the thermal conductivity.

Example 5: Radiation-Reflecting Inorganic Particles in Hydrogel

Example 5a: Scattering Efficiency of Radiation-Reflecting Inorganic Particles

Scattering effect on $BaSO_4$ nanoparticle boundary was evaluated by Finite-Difference Time-Domin (FDTD) simulations. Typical refractive index of air and $BaSO_4$ (1 and 1.63, respectively) were used in the analysis. Scattering cross section of a single nanoparticle was calculated and considered to be the scattering efficiency after division of cross-section length with total-field scattered-field (TFSF) and perfect matching layer (PML) boundary conditions. Sweeping analysis (Figure 7c) was conducted for comprehensive evaluation of UV-vis-NIR range scattering upon various particle sizes (from 0.1 to 1.0 μm).

Calculated result indicates that particles with diameters from 200 to 400 nm broadly scatter UV-vis-NIR light, which mainly comes from the comparable size with wavelength, also known as Mie scattering. Correspondingly, particles with average size of 350 nm were applied as light scatter agents in hydrogel (as shown Figure 7d), where the UV-vis reflection outcome upon particle addition was proved to be efficient (Figure 11a to Figure 11c). Figure 11a to Figure 11c show an optical performance of Metagel-2. Also shown in Figure 11c, the results of the comparison of solar reflectance and transmittance of Metagel-2 with different thicknesses is shown in Table 4.

Price / Components	Average Content (g/cm^3)	Unit Price of Product (SGD/kg)	Specific Expense (SGD/cm^3)	Total Expense (SGD/m^2*mm)
50% Glutaraldehyde Solution	~0.037	~3.2	~$1.184*10^{-4}$	Metagel-4: ~0.942
Sulfuric Acid	~0.107	~0.18	~$0.192*10^{-4}$	

Example 6: Biocompatibility Test of Hydrogels

Biocompatibility test is conducted to determine the toxicity, and biocompatibility of the hydrogels. This biocompatibility test is important to assess and determine whether the hydrogels are suitable for safe use and applications. Figure 10a to Figure 10d show the biocompatibility and use of skin cooling using Metagel-2.

For bio-compatibility test (Figure 10a), the Metagel-2 was immersed in the standard culture medium overnight in the 60 × 15mm Petri dishes (Sigma-Aldrich). Fibroblast (NIH/3T3, ATCC-CRL-1658) cells were seeded and cultured on the surface of Metagel-2. The cells were trypsinized in time steps of 0, 24, and 72-hour to check viability with trypan blue (CAT:15250061, Thermo Fisher Scientific) in the cell counter (Countess, Thermo Fisher Scientific).

Figure 10a shows that the concentration of NIH-3T3 fibroblast cell of Metagel-2 is similar to the control and that the cells concentration increases over time. This indicates that the Metagel-2 is a non-hazardous, biocompatible and non-toxic material for skin.

Example 7: Thermal Analysis of Hydrogels

To rationalize the inventors' experimental observations, a 2D axisymmetric model is firstly adopted based on the experimental set-up, as shown in Figure 15 (a). The rectangular domain has a radius of R_{gel} and a height of $H_{\mathrm{gel}} + H_{\mathrm{EPS}}$, where EPS represents expanded polystyrene. The volume fraction of each phase is θ and they fulfill the following constraint, i.e.,

$$\theta_{\mathrm{S}} + \theta_{\mathrm{L}} + \theta_{\mathrm{G}} = 1 \qquad (1)$$

where the index S, L, and G are used for the solid, liquid, and gaseous phases, i.e., the Metagel-2 containing particles, water, and air in this model, respectively.

Claims

1. A method of preparing a hydrogel, comprising:

(i) preparing a mixture of water-soluble polymer, inorganic acid, and radiation-reflecting inorganic particles;

(ii) adding a crosslinking agent to the mixture to form a hydrogel precursor;

(iii) freezing and thawing the hydrogel precursor thereby forming a hydrogel,

wherein the hydrogel precursor comprises:

5 wt% to 30 wt% of water-soluble polymer;

0.3 wt% to 2.5 wt% of inorganic acid;

0.05 wt% to 0.5 wt% of crosslinking agent; and

3 wt% to 67 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor, and

wherein the radiation-reflecting inorganic particle is barium sulfate.

2. The method of claim 1, wherein the hydrogel precursor comprises:

5 wt% to 25 wt% of water-soluble polymer;

0.3 wt% to 1.2 wt% of inorganic acid;

0.05 wt% to 0.25 wt% of crosslinking agent; and

30 wt% to 67 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor

3. The method of claim 1 or 2, wherein step (iii) is repeated at least once.

4. The method of any one of claims 1 to 3, wherein chemical crosslinks within the hydrogel are formed in step (ii).

5. The method of any one of claims 1 to 4, wherein physical crosslinks within the hydrogel are formed in step (iii).

6. The method of any one of claims 1 to 5, wherein the hydrogel comprises a framework comprising crosslinked polymeric chains that form a polymeric matrix, radiation-reflecting inorganic particles homogenously distributed in the polymeric matrix, and hydrogen bonds between the radiation-reflecting inorganic particles, and the polymeric matrix.

7. The method of any one of claims 1 to 6, wherein step (i) is performed at a pH of 1 or lower.

8. The method of any one of claims 1 to 7, wherein step (i) comprises:

(ia) preparing a mixture of inorganic acid and radiation-reflecting inorganic particles to form a dispersion;

(ib) mixing the dispersion with water-soluble polymer.

9. The method of any one of claims 1 to 8, wherein step (iii) comprises freezing the mixture at a temperature of -40 °C to -20 °C for a duration of 6 hours to 12 hours.

10. The method of any one of claims 1 to 9, wherein step (iii) comprises thawing the mixture at a temperature of 20 °C to 30 °C for a duration of 0.5 hours to 3.5 hours.

11. The method of any one of claims 1 to 10, wherein the molecular weight (MW) of the water-soluble polymer is 70,000 to 100,000 and/or at least 97.5% to 99.5% hydrolyzed.

12. The method of any one of claims 1 to 11, wherein the water-soluble polymer is selected from the group consisting of poly(vinyl alcohol) (PVA), sodium alginate, gelatin, polyacrylic acid, chitosan, cellulose and polyacrylamide.

13. The method of any one of claims 1 to 12, wherein the inorganic acid is selected from the group consisting of hydrochloric acid, chloric acid, sulfuric acid, phosphoric acid, and nitric acid.

14. The method of any one of claims 1 to 13, wherein the crosslinking agent is selected from the group consisting of glutaraldehyde, calcium chloride ($CaCl_2$), sodium triphosphate, N-N'-methylenebisacrylamide ($C_7H_{10}N_2O_2$), acetic acid, cucurbit[7]uril ($C_{42}H_{42}N_{28}O_{14}$), and combinations thereof.

15. The method of any one of claims 1 to 14, wherein the radiation-reflecting inorganic particle has an average diameter of 0.1 μm to 1 μm.

16. A hydrogel obtained by the method of any one of claims 1 to 15.

17. The hydrogel of claim 16, wherein the hydrogel comprises chemical and physical crosslinks.

18. The hydrogel of claim 16 or 17, wherein the hydrogel comprises a framework comprising crosslinked polymeric chains that form a polymeric matrix, radiation-reflecting inorganic particles homogenously distributed in the polymeric matrix, and hydrogen bonds between the radiation-reflecting inorganic particles, and the polymeric matrix.

19. The hydrogel of any one of claims 16 to 18, wherein the hydrogel comprises 20 wt% to 50 wt% of water based on the total weight of hydrogel.

20. The hydrogel of any one of claims 16 to 19, wherein the hydrogel comprises at least 15 wt% to 45 wt% of free water and intermediate water based on the total weight of the hydrogel.

21. The hydrogel of any one of claims 16 to 20, wherein the hydrogel comprises pores with an average pore diameter of 1 μm to 10 μm.

22. The hydrogel of any one of claims 16 to 21, wherein the hydrogel has a thickness of 1 mm to 20 mm.

23. The hydrogel of any one of claims 16 to 22, wherein the hydrogel comprises PVA and glutaraldehyde.

24. A hydrogel prepared by freeze-thawing a hydrogel precursor, wherein the hydrogel precursor comprises:

5 wt% to 30 wt% of water-soluble polymer;
0.3 wt% to 2.5 wt% of inorganic acid;
0.05 wt% to 0.5 wt% of crosslinking agent; and

3 wt% to 67 wt% of a radiation-reflecting inorganic particle,

or

5 wt% to 25 wt% of water-soluble polymer;
0.3 wt% to 1.2 wt% of inorganic acid;
0.05 wt% to 0.25 wt% of crosslinking agent; and
30 wt% to 67 wt% of a radiation-reflecting inorganic particle,

wherein the wt% is based on the total weight of the hydrogel precursor, and wherein the radiation-reflecting inorganic particle is barium sulfate.

25. A fabric-supported hydrogel comprising a fabric and the hydrogel of any one of claims 16 to 24.

26. The fabric-supported hydrogel of claim 25, wherein the fabric-supported hydrogel has a framework comprising a fabric skeleton, crosslinked polymeric chains that form a polymeric matrix, radiation-reflecting inorganic particles homogenously distributed in the polymeric matrix, and hydrogen bonds between the radiation-reflecting inorganic particles, the polymeric matrix and the fabric skeleton.