

METHOD OF REMOVING HEAT ENERGY FROM AN OBJECT

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore patent application No. 201308215-1 filed on 5 November 2013, the content of which is incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] The invention relates to a method of removing heat energy from an object.

BACKGROUND

[0003] Current methods to remove heat energy from buildings, thereby lowering temperature in the buildings are costly and non-environmentally friendly. For example, air-conditioners are commonly used to remove heat from a space using a vapor-compression refrigeration cycle. As electricity is required to power the air-conditioners, it is energy and cost intensive. The heat removed is disposed as waste heat outside the building, thereby increasing temperature of the exterior environment. The air-conditioners also release greenhouse gases into the environment.

[0004] Although roof gardens are able to reduce temperature of buildings via evaporative cooling, they add significant mass which result in high stress to the roof as well as pillars. Furthermore, roof gardens cannot conveniently be added to existing buildings.

[0005] In view of the above, there exists a need for improved methods of removing heat energy from objects such as buildings that overcome or at least alleviate one or more of the above-mentioned problems.

SUMMARY

[0006] In a first aspect, a method of removing heat energy from an object is provided. The method comprises

- a) providing a hydrated hydrogel having a lower critical solution temperature of about 70 °C or less,
- b) thermally contacting the hydrated hydrogel with an object, and

- c) allowing water to evaporate from the hydrated hydrogel, thereby removing heat energy from the object.

[0007] In a second aspect, use of a hydrated hydrogel having a lower critical solution temperature of about 70 °C or less in removing heat energy from an object is provided.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

10 [0009] **FIG. 1A** is a schematic diagram showing a top view of experimental set-up described in the examples.

[0010] **FIG. 1B** is a schematic diagram showing a side view of experimental set-up described in the examples.

[0011] **FIG. 2** is a graph showing temperature of 5 % hydroxypropyl cellulose (HPC) solution (averaged between 2 samples) with respect to time when heated. The experimental set-up used is shown in **FIG. 1A** and **FIG. 1B**, with the ambient temperature set at 100 °C. Three thermocouples were used to measure a) ambient temperature; b) temperature of cup 1 containing HPC solution; c) temperature of cup 2 containing HPC solution. Temperatures of the samples did not rise above 70 °C, attesting to the evaporative cooling effect of the polymer solution.

[0012] **FIG. 3** is a graph showing temperature of HPC gel versus water with respect to time when heated under similar conditions as that used for generating **FIG. 2**.

[0013] **FIG. 4** is a graph showing temperature of thermogel poly(PEG/PPG/PHB urethane) with respect to time when heated under similar conditions as that used for generating **FIG. 3**.

25 The ambient temperature remained at about 70 ± 0.3 °C after the first two minutes.

DETAILED DESCRIPTION

[0014] When temperature of the surroundings is high, such as during the day, temperature of a hydrated hydrogel may increase beyond its lower critical solution temperature (LCST).

30 At temperatures at or above its LCST, phase separation occurs, and polymer chains within the hydrogel associate preferentially with themselves rather than with water molecules. As a result, water may be evaporated easily. Since water has a high latent heat of vaporization, the

evaporation of water removes a substantial amount of heat energy from a surface of an object it is in thermal contact with. This in turn leads to a decrease in temperature of the object.

[0015] Conversely, when temperature of the surroundings is low, such as during the night or on a rainy day, temperature of the hydrogel may decrease below its LCST. The hydrogel may remain in a solid gel form to allow better water retention. As relative humidity of air may be as high as 95 % at such conditions, the hydrogel may absorb water vapor from ambient air, thereby replenishing water that is lost from evaporative cooling when temperature of the surroundings is high, such as during the day. Similarly, rain water may be channeled to hydrate the hydrogel.

[0016] Through this evaporative cooling mechanism of hydrogels, temperature of objects that are in thermal contact with the hydrogels may be reduced in an environmentally friendly manner. An evaporative cooling system disclosed herein may operate and regenerate passively, as electricity or other sources of energy are not required. It is also a 'smart' system because rate of evaporation is higher when the weather is hot and sunny, and lower when the weather is cool and cloudy. Advantageously, use of hydrogel as a water-retainer allows the evaporation process to be carried out over a longer period of time, which in turn leads to an extended duration for cooling.

[0017] With the above in mind, various embodiments refer in a first aspect to a method of removing heat energy from an object.

[0018] The method includes providing a hydrated hydrogel having a lower critical solution temperature of about 70 °C or less, thermally contacting the hydrated hydrogel with an object, and allowing water to evaporate from the hydrated hydrogel, thereby removing heat energy from the object.

[0019] As used herein, the term "hydrogel" refers to a broad class of polymeric materials, which may be natural or synthetic, having affinity for an aqueous medium in that they are able to absorb large amounts of the aqueous medium, but do not normally dissolve in the aqueous medium. The term "aqueous medium" as used herein refers to water or a solution based primarily on water such as phosphate buffered saline (PBS), or water containing a salt dissolved therein.

[0020] Hydrogels have excellent water retention properties as they contain hydrophilic groups which allow absorption of a large amount of water. Generally, a hydrogel may be formed using at least one, or one or more types of hydrogel precursor, and setting or

solidifying the one or more types of hydrogel precursor in an aqueous solution to form a three-dimensional network, wherein formation of the three-dimensional network may cause the one or more types of hydrogel precursor to gel.

[0021] The term “hydrogel precursor” refers to any chemical compound that may be used to make a hydrogel. Examples of hydrogel precursors include, but not limited to, a natural polymer, a hydrophilic monomer, a hydrophilic polymer, a hydrophilic copolymer formed from a monomer and a polymer.

[0022] In various embodiments, the hydrogel precursor is a hydrophilic polymer capable of forming a hydrogel when contacted with an aqueous medium such as water. The hydrophilic polymer may be a polymer which is formed from and/or made up of hydrophilic monomers, and which may be formed from any reaction such as, but not limited to, free radical polymerization, condensation polymerization, anionic or cationic polymerization, or step growth polymerization.

[0023] Examples of hydrophilic monomers include, but are not limited to, hydroxyl-containing monomers such as 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylamide, 2-hydroxyethyl acrylamide, N-2-hydroxyethyl vinyl carbamate, 2-hydroxyethyl vinyl carbonate, 2-hydroxypropyl methacrylate, hydroxyhexyl methacrylate and hydroxyoctyl methacrylate; carboxyl-containing monomers such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, maleic acid and salts thereof, esters containing free carboxyl groups of unsaturated polycarboxylic acids, such as monomethyl maleate ester, monoethyl maleate ester, monomethyl fumarate ester, monoethyl fumarate ester and salts thereof; amide-containing monomers such as (meth)acrylamide, crotonic amide, cinnamic amide, maleic diamide and fumaric diamide; thiol-containing monomers such as methanethiole, ethanethiol, 1-propanethiol, butanethiol, tert-butyl mercaptan, and pentanethiols; sulfonic acid-containing monomers such as p-styrenesulfonic acid, vinylsulfonic acid, p-a-methylstyrenesulfonic acid, isoprene sulfonide and salts thereof.

[0024] The hydrogel precursor may be a hydrophilic copolymer. The hydrophilic copolymer may be formed from a hydrophilic polymer and a monomer which may be hydrophilic, hydrophobic, or amphiphilic. In some embodiments, a hydrophilic copolymer may be formed from a hydrophilic monomer and a polymer which may be hydrophilic, hydrophobic or amphiphilic. For example, a hydrophobic monomer may react with a functional group present on a hydrophilic polymer to form a hydrophilic copolymer.

[0025] One or more types of hydrogel precursors may set or solidify in an aqueous medium to form a three-dimensional network, wherein formation of the three-dimensional network may cause the one or more types of hydrogel precursor to gel. For example, a hydrogel may be formed by physical bonding such as self assembly, or chemical bonding such as cross-linking, of one or more types of hydrogel precursors in an aqueous medium.

[0026] The hydrated hydrogel has a lower critical solution temperature of about 70 °C or less. The term “lower critical solution temperature”, or LCST, refers to the maximum temperature at which a polymer changes from a state of being soluble in an aqueous medium such as water to a state of being insoluble in the aqueous medium. This temperature is characteristic for a particular substance. It is also a transition temperature of the polymer between hydration and dehydration. At a temperature lower than this temperature, the polymer molecule is hydrated and molecule chain of the polymer is expanded, while at a temperature higher than this temperature, dehydration occurs and the molecular chain aggregates. These changes which are due to temperature are reversible.

[0027] Examples of hydrogels having a lower critical solution temperature of about 70 °C or less include, but are not limited to, hydrogels made from a cellulose-based polymer, hydrogels made from an urethane-based polymer, and hydrogels made from a mixture and/or a copolymer of a cellulose-based polymer and an urethane-based polymer. These hydrogels are particularly suitable for use in a method of removing heat energy disclosed herein.

[0028] Examples of cellulose-based polymers that may be used to form hydrogels having a lower critical solution temperature of about 70 °C or less include methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, N-isopropylacrylamide grafted cellulose, semi-interpenetration network of sodium carboxymethylcellulose and N-isopropylacrylamide, mixtures thereof, and copolymers thereof.

[0029] Examples of urethane-based polymers that may be used to form hydrogels having a lower critical solution temperature of about 70 °C or less include polyurethane multiblock copolymers of poly(propylene glycol), poly(ethylene glycol), and polycaprolactone, and polyurethane multiblock copolymers of poly[(R)-3-hydroxybutyrate], poly(ethylene glycol) and poly(propylene glycol), mixtures thereof, and copolymers thereof.

[0030] In various embodiments, the hydrogel is selected from the group consisting of hydrogels made from a cellulose-based polymer, hydrogels made from an urethane-based

polymer, hydrogels made from mixtures or copolymers of a cellulose-based polymer and an urethane-based polymer, and combinations thereof.

[0031] In some embodiments, the hydrogel comprises or consists of a hydrogel made from hydroxypropyl cellulose (HPC).

5 [0032] Hydroxypropyl cellulose is a derivative of cellulose, specifically an ether of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxypropylated to form $-OCH_2CH(OH)CH_3$ groups using propylene oxide. HPC has a lower critical solution temperature (LCST) of about 45 °C, hence at temperatures below the LCST, HPC is readily soluble in water, whereas at temperatures above the LCST, HPC is not
10 soluble in water.

[0033] In some embodiments, the hydrogel comprises or consists of a hydrogel made from an amphiphilic multiblock polyether/polyester urethane, wherein (i) the polyether optionally comprises or consists of polyethylene glycol and/or polypropylene glycol, and/or (ii) the polyester optionally comprises or consists of polyhydroxybutyrate. Examples of such
15 amphiphilic multiblock polyether/polyester urethanes are provided, for example, in WO 2007/117222 and US 20130018111.

[0034] In various embodiments, the hydrogel is formed by self-assembly of one or more types of hydrogel precursors in an aqueous medium. The term “self-assembly” refers to a process of spontaneous organization of components of a higher order structure by reliance on
20 the attraction of the components for each other, and without chemical bond formation between the components. For example, polymer chains may interact with each other via any one of hydrophobic forces, hydrogen bonding, Van der Waals interaction, electrostatic forces, or polymer chain entanglement, induced on the polymer chains, such that the polymer chains may aggregate or coagulate in an aqueous medium, which may form a three-dimensional
25 network, thereby entrapping molecules of water to form a hydrogel.

[0035] In some embodiments, the hydrogel may be formed by chemical bonding between one or more types of hydrogel precursors in an aqueous medium. For example, when the hydrogel precursor is a hydrophilic polymer, the polymeric chains may be cross-linked using a suitable cross-linking agent to form a three-dimensional network, which may entrap water
30 molecules to form a hydrogel.

[0036] The term “cross-link” as used herein refers to an interconnection between polymer chains via chemical bonding, such as, but not limited to, covalent bonding, ionic bonding, or

affinity interactions (e.g. ligand/receptor interactions, antibody/antigen interactions, etc.). The chemical cross-linking may be carried out by reactions, such as any one of free radical polymerization, condensation polymerization, anionic or cationic polymerization, or step growth polymerization.

5 [0037] The hydrogel may be cross-linked with a cross-linking agent. As used herein, the term "cross-linking agent" refers to an agent which induces cross-linking. The cross-linking agent may be any agent that is capable of inducing a chemical bond between adjacent polymeric chains.

[0038] For example, the cross-linking agent may be a chemical compound. Examples of
10 chemical compounds that may act as cross-linking agent include, but are not limited to, glyoxal, glutaraldehyde, polyethylene glycol diglycidyl ether, divinyl sulfone, epichlorohydrin, 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC), vinylamine, 2-aminoethyl methacrylate, 3-aminopropyl methacrylamide, ethylene diamine, ethylene glycol dimethacrylate, methymethacrylate, N,N'-methylene-bisacrylamide, N,N'-
15 methylene-bis-methacrylamide, diallyltartardiamide, allyl(meth)acrylate, lower alkylene glycol di(meth)acrylate, poly lower alkylene glycol di(meth)acrylate, lower alkylene di(meth)acrylate, divinyl ether, divinyl sulfone, di- or trivinylbenzene, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, bisphenol A di(meth)acrylate, methylenebis(meth)acrylamide, triallyl phthalate, diallyl phthalate, transglutaminase or
20 mixtures thereof.

[0039] In various embodiments, the hydrogel is cross-linked with a cross-linking agent selected from the group consisting of glyoxal, glutaraldehyde, polyethylene glycol diglycidyl ether, divinyl sulfone, epichlorohydrin, and combinations thereof. In some embodiments, the hydrogel is cross-linked with glyoxal.

25 [0040] In some embodiments, the cross-linking agent may be in the form of an electromagnetic wave. Therefore, cross-linking may be carried out using an electromagnetic wave, such as gamma or ultraviolet radiation, which may cause the polymeric chains to cross-link and form a three-dimensional matrix, thereby entrapping water molecules to form a hydrogel.

30 [0041] As mentioned above, the hydrated hydrogel has a lower critical solution temperature lower than about 70 °C. In various embodiments, the hydrated hydrogel has a lower critical solution temperature of about 60 °C or less, such as about 50 °C or less, about

45 °C or less, about 30 °C or less, about 25 °C or less, about 20 °C or less, about 15 °C to about 70 °C, about 25 °C to about 65 °C, about 30 °C to about 50 °C, or about 40 °C to about 50 °C. In specific embodiments, the hydrated hydrogel has a lower critical solution temperature of about 45 °C or less.

5 [0042] Without wishing to be bound by theory, according to Qiang Fu (*Fu, Q., 2002: Solar Radiation. Encyclopedia of Atmospheric Sciences (Edited by J. Holton, J. Pyle, and J. Curry), Academic Press, 1859-1863*), analysis of satellite data suggests that the solar constant, which is the amount of solar radiation received outside the Earth's atmosphere on a surface normal to the incident radiation received outside the Earth's atmosphere on a surface
10 normal to the incident radiation per unit time per unit area, to be 1366 Wm^{-2} . Radiation is reflected away by the atmosphere, and absorbed by clouds, and the annual global mean radiation absorbed at the Earth's surface is 168 Wm^{-2} . This equates to an average of 14.5 MJ m^{-2} of heat energy absorbed over a period of 24 hours.

[0043] Since hydrogels become white when phase separation occurs, and white materials
15 have a high reflective coefficient, it was postulated that hydrogels do not absorb more than 10 MJ m^{-2} of solar radiation every 24 hours. As water has a latent heat of vaporization of 2.3 MJ kg^{-1} , 4 kg of water per m^2 of surface is able to remove energy from sun's radiation, assuming that the rate of evaporation is sufficient. It follows that a hydrogel layer in the order of millimeters, such as 1000 mm or less, 800 mm or less, 500 mm or less, or 300 mm or less,
20 may be able to hold this amount of water. Having a thicker layer of hydrogel is advantageous as it is possible to retain a greater amount of water, and hence able to maintain evaporative cooling for extended duration during dry periods.

[0044] By the term "hydrated hydrogel", it means that the hydrogel may be substantially composed of water. The amount of water in the hydrated hydrogel may be at least 50 wt%, at
25 least 55 wt%, at least 60 wt%, at least 65 wt%, at least 70 wt%, at least 75%, at least 80 wt%, at least 85%, at least 90%, or at least 95%, wherein weight percentage is expressed as weight of water with respect to total weight of the hydrated hydrogel. The term "hydrated hydrogel" includes partially-hydrated hydrogels, wherein the term "partially-hydrated hydrogel" describes a hydrogel containing some amounts of water and which is able to take in or
30 receive additional quantities of water. For example, amount of water in a partially-hydrated hydrogel may be less than 50 wt%, such as 40 wt% or less, 30 wt% or less, or 20 wt% or less. The term "non-hydrated hydrogel", on the other hand, means that the hydrogel contains

negligible amounts of water, such as 5 wt% or less, or 3 wt% or less water, or may not contain any water.

[0045] The hydrated hydrogel is thermally contacted with an object. By the term “thermally contacting”, this means that the hydrated hydrogel is arranged to allow transfer of heat energy from the object to the hydrated hydrogel. For example, the hydrated hydrogel may contact the object directly, or via a heat conductor such as a metal. In so doing, heat energy from the object may transfer from the object to the hydrated hydrogel, so as to remove heat energy from the object by way of the evaporating water. In various embodiments, thermally contacting the hydrated hydrogel with the object comprises directly contacting the hydrated hydrogel with the object.

[0046] The object may be an object where heat energy is to be removed. Examples of the object may include, but not limited to, an equipment, a display, an electronic device, a furniture, a vehicle, a structure, a fabric, an article of clothing, a building component, a building, and combinations thereof.

[0047] In various embodiments, the object is a building. As discussed above, water is allowed to evaporate from the hydrated hydrogel, thereby removing heat energy from the object that is in thermal contact with the hydrogel. Through evaporative cooling of hydrogels, temperature within buildings may be reduced in an environmentally friendly manner.

[0048] As mentioned above, the hydrogel may absorb water vapor from ambient air, especially in cases where relative humidity of air is high. In addition, rain water may be directed to the hydrogel to aid in replenishing water that is lost during evaporation. Taking Singapore for example, average monthly precipitation of Singapore is approximately 200 mm. Hence, by collecting and directing rainwater to the hydrogel, an additional water supply is not required to replenish water that is lost from the hydrated hydrogel by evaporation. In various embodiments, providing the hydrated hydrogel comprises exposing a non-hydrated or a partially-hydrated hydrogel having a lower critical solution temperature lower than about 70 °C to ambient water vapor or rain water to hydrate the hydrogel.

[0049] The method of removing heat energy from an object disclosed herein may be used independently on its own, or in tandem with other methods or devices of heat energy removal. For example, buildings may be simultaneously cooled by air-conditioners as well as evaporative cooling of hydrogel disclosed herein to reduce energy costs. In various

embodiments, providing the hydrated hydrogel comprises arranging the hydrated hydrogel on a highly reflective surface. In so doing, greater cooling effects may be achieved.

[0050] In various embodiments, the hydrated hydrogel may be provided by arranging the hydrated hydrogel in an enclosure, wherein at least one side of the enclosure is covered with a waterproof membrane. In some embodiments, one side of the enclosure is covered with a waterproof membrane. The membrane may be partially or at least substantially porous, so as to allow evaporation of water from the hydrated hydrogel, while protecting the hydrogel from weather elements.

[0051] The hydrogel may also act as a matrix or framework for additional components.

Examples of such additional components include a biocide or an algacide. The hydrogel support may covalently bind or non-covalently entrap the additional materials. In various embodiments, providing a hydrated hydrogel having a lower critical solution temperature lower than 70 °C comprises adding at least one of a biocide or an algacide to hydrogel precursors prior to gelation of the hydrogel precursors to form the hydrated hydrogel.

[0052] In a further aspect, use of a hydrated hydrogel having a lower critical solution temperature lower than about 70 °C in removing heat energy from an object is provided. The object may be an equipment, a display, an electronic device, a furniture, a vehicle, a structure, a fabric, an article of clothing, a building component, and/or a building, to name only a few.

[0053] As mentioned above, although roof gardens are also able to reduce temperatures in buildings via evaporative cooling, they add significant mass and hence result in high stress to the roof as well as pillars. Furthermore, roof gardens cannot be conveniently added to existing buildings. On the other hand, mass of a hydrogel layer in the order of millimeters is significantly lower than that of roof gardens, and a hydrogel layer may be conveniently fitted to roofs of almost any geometry.

[0054] Advantageously, hydrogels such as cellulose-based hydrogels are environmentally friendly and readily available at a low cost. They may be synthesized quickly and easily, and the product may be fitted to existing buildings with ease. Therefore, embodiments of a cooling system disclosed herein may be adopted for use on a large scale.

[0055] Hereinafter, the present invention will be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein. Rather, these

embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, lengths and sizes of layers and regions may be exaggerated for clarity.

[0056] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0057] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0058] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0059] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups,

those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

EXPERIMENTAL SECTION

[0060] Preparation of cellulose-based hydrogel for the purpose of evaporative cooling, in particular for decreasing the temperature of buildings in an environmentally friendly manner is disclosed herein. Such a cooling system is able to operate and regenerate passively by retaining rainwater, and is also a 'smart' system because the rate of evaporation varies with the ambient temperature. Cellulose-base hydrogels may be synthesized easily and are available at a low cost, and may be coupled with existing cooling methods such as reflective roofing or roof lawn gardens.

[0061] Evaporative cooling effects of various cellulose-based and non-cellulose-based polymer solutions and gels according to various embodiments were tested. In the experiments carried out, the cellulose-based and non-cellulose-based polymer solutions and gels were heated using a solar lamp in a controlled environment under similar conditions, and their temperature versus that of ambient temperature was measured using a thermocouple.

[0062] Performances of different polymer solutions were compared. From the results obtained, hydroxypropyl cellulose (HPC) was determined to be favorable for evaporative cooling gels. Without wishing to be bound by theory, this may be attributed to the low lower critical solution temperature (LCST) of HPC, whereby its phase separation takes place at a lower temperature, and hence earlier, than other polymer solutions. HPC-based hydrogels were further tested for evaporative cooling. Use of thermogelling high molecular weight amphiphilic multiblock poly(ether ester urethane)s formed of PEG, PPG and PHB blocks for evaporative cooling was also studied.

[0063] **Example 1: Method (a) – Corresponds to EC57(a), tested in EC55c and EC55f**

[0064] 3.0 g of HPC (M_w 370,000) powder, 12.6 g of 40 wt% glyoxal in water H_2O , and 0.75 g of 37 % hydrochloric acid (HCl) was added to 9.0 g of deionized water and the mixture was blended thoroughly using a homogenizer. The product was then heated at 80 °C for 30 minutes. Deionized water was further added to swell the hydrogel.

[0065] **Example 2: Method (b) – Corresponds to EC42(a), tested in EC55b and EC55e**

[0066] To 15.1 g of 40 wt% glyoxal, 0.31 g of HPC (M_w 370,000) powder and 0.3130 g of 10 wt% PAA (M_w 450,000) solution were added and stirred manually. Then, 5 drops of 37 wt% HCl was added to the mixture, and heated in a 60 °C water bath. While curing, 10 wt% HPC (M_w 370,000) solution was added and stirred. Then, the mixture was heated in a 90 °C water bath for 30 minutes. The white solid gel was removed from the solution and retained. Deionized water was used to wash and swell the hydrogel.

[0067] **Example 3: Synthesis of Poly(PEG/PPG/PHB urethane)s**

[0068] Telechelic hydroxylated PHB (PHB-diol) prepolymers with various molecular weight were prepared by transesterification between the natural source PHB and ethylene glycol using dibutyltin dilaurate in diglyme. The yields were about 80 %.

[0069] Poly(PEG/PPG/PHB urethane)s were synthesized from PHB-diol, PEG, and PPG using 1,6-hexamethylene diisocyanate (HDI) as a coupling reagent. The amount of HDI added was equivalent to the reactive hydroxyl groups in the solution. Typically, 0.064 g of PHB-diol ($M_n = 1070$, 6.0×10^{-5} mol), 1.44 g of PEG ($M_n = 1890$, 7.6×10^{-4} mol), and 0.82 g of PPG ($M_n = 2180$, 3.8×10^{-4} mol) were dried in a 250-mL two-neck flask at 50 °C under high vacuum overnight. Then, 20 mL of anhydrous 1,2-dichloroethane was added to the flask, and any trace of water in the system was removed through azeotropic distillation with only 1 mL of 1,2-dichloroethane being left in the flask.

[0070] When the flask was cooled down to 75 °C, 0.20 g of HDI (1.2×10^{-3} mol) and two drops of dibutyltin dilaurate (8×10^{-3} g) were added sequentially. The reaction mixture was stirred at 75 °C under a nitrogen atmosphere for 48 h. The resultant copolymer was precipitated from diethyl ether, and further purified by redissolving into 1,2-dichloroethane followed by precipitation in a mixture of methanol and diethyl ether to remove remaining dibutyltin dilaurate.

[0071] **Example 4: Method of testing evaporative cooling by hydrogels**

[0072] The samples were heated in a solar chamber (see FIG. 1A and FIG. 1B), which models a controlled environment, instead of being heated in the open. A lamp is fixed inside the chamber, and a thermocouple control is used to keep the temperature of a chosen reference point at a specific temperature. The lamp is switched on until the thermocouple registers the reference point to be at the desired temperature, and then switched off, and the process repeated whenever the temperature deviates. Therefore, the temperature is maintained by the automatic control of the lamp.

[0073] In embodiments, the solid hydrogels were heated in a controlled environment, maintained at a temperature of 70 °C by a 150 W IR lamp, for 90 minutes.

[0074] The position of each sample was marked, so that the incident irradiation on each sample is the same for subsequent experiments. Hence, a fair comparison can be made between different solutions or gels, and with deionized water as a control.

[0075] The polymer solutions were placed in a self-made aluminum cup, with the sides insulated by parafilm and tape. This was done to allow better thermal conductivity between the polymer solution and the thermocouple, so that the temperature displayed by the thermocouple was a more accurate indication of the polymer temperature. In addition, thermal grease was used for better thermal contact between the thermocouple and the cup. Care was taken to reduce thermal conduction by the side of the cup, to avoid heat being conducted directly via the sides resulting in erroneous temperature measurements. To decrease random error, each experiment involved two samples of the same polymer solution, and average temperature of the two readings was taken.

[0076] Results showed that the temperature of hydrogel was only about 2 °C higher than that of water when heated under similar conditions. Therefore, hydrated cellulose-based hydrogels have evaporative cooling properties similar to water itself.

[0077] Various embodiments as disclosed herein are significant as they are able to help alleviate issues associated with removal of heat energy or cooling of objects, which are particularly pertinent to a hot climate such as that of Singapore's, in a simple, cheap and environmentally friendly manner. The product may be in the form of layers of solid hydrogel, placed in troughs and packaged within breathable water proof membrane to protect the hydrogel from the weather elements. Channels may be present to direct rainwater to the hydrogel.

[0078] Advantageously, using hydrogel as a means for storing water is better than rainwater collection in a vessel, for example, because the latter may result in breeding of mosquitoes due to stagnant water. In addition, use of hydrogel as a water-retainer allows the water evaporation process to be carried out over a longer period of time, which in turn leads to an extended cooling duration. This evaporative cooling system may operate and regenerate passively, and is also a 'smart' system because rate of evaporation is higher when the weather is hot and sunny, and lower when the weather is cool and cloudy.

[0079] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

CLAIMS

1. A method of removing heat energy from an object, the method comprising
 - a) providing a hydrated hydrogel having a lower critical solution temperature of
5 70 °C or less, wherein providing the hydrated hydrogel comprises adding at least one of a biocide or an algacide to hydrogel precursors prior to gelation of the hydrogel precursors to form the hydrated hydrogel,
 - b) thermally contacting the hydrated hydrogel with an object, and
 - c) allowing water to evaporate from the hydrated hydrogel, thereby removing
10 heat energy from the object.
2. The method according to claim 1, wherein providing the hydrated hydrogel comprises exposing a non-hydrated or a partially-hydrated hydrogel having a lower critical solution temperature lower than 70 °C to ambient water vapor or rain water to hydrate
15 the hydrogel.
3. The method according to claim 1 or 2, wherein thermally contacting the hydrated hydrogel with an object comprises arranging the hydrated hydrogel on a reflective surface of the object.
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4. The method according to any one of claims 1 to 3, wherein providing the hydrated hydrogel comprises arranging the hydrated hydrogel in an enclosure, wherein at least one side of the enclosure is covered with a waterproof membrane.
- 25 5. The method according to any one of claims 1 to 4, wherein the hydrogel is selected from the group consisting of hydrogels made from a cellulose-based polymer, hydrogels made from an urethane-based polymer, hydrogels made from mixtures or copolymers of a cellulose-based polymer and an urethane-based polymer, and combinations thereof.

6. The method according to claim 5, wherein the cellulose-based polymer is selected from the group consisting of methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, N-isopropylacrylamide grafted cellulose, semi-interpenetration network of sodium carboxymethylcellulose and N-isopropylacrylamide, mixtures thereof, and copolymers thereof.
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7. The method according to claim 5 or 6, wherein the urethane-based polymer is selected from the group consisting of polyurethane multiblock copolymers of poly(propylene glycol), poly(ethylene glycol), and polycaprolactone, polyurethane multiblock copolymers of poly[(R)-3-hydroxybutyrate], poly(ethylene glycol), and poly(propylene glycol), mixtures thereof, and copolymers thereof.
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8. The method according to any one of claims 1 to 7, wherein the hydrogel comprises or consists of a hydrogel made from hydroxypropyl cellulose (HPC).
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9. The method according to any one of claims 1 to 8, wherein the hydrogel comprises or consists of a hydrogel made from an amphiphilic multiblock polyether/polyester urethane, wherein (i) the polyether optionally comprises or consists of polyethylene glycol and/or polypropylene glycol, and/or (ii) the polyester optionally comprises or consists of polyhydroxybutyrate.
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10. The method according to any one of claims 1 to 9, wherein the hydrogel is cross-linked with a cross-linking agent selected from the group consisting of glyoxal, glutaraldehyde, polyethylene glycol diglycidyl ether, divinyl sulfone, epichlorohydrin, and combinations thereof.
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11. The method according to any one of claims 1 to 10, wherein the hydrogel is cross-linked with glyoxal.
- 30 12. The method according to any one of claims 1 to 11, wherein the lower critical solution temperature of the hydrated hydrogel is 45 °C or less.

13. The method according to claim 1, wherein thermally contacting the hydrated hydrogel with the object comprises directly contacting the hydrated hydrogel with the object.

14. The method according to any one of claims 1 to 13, wherein the object is selected from the group consisting of an equipment, a display, an electronic device, a furniture, a vehicle, a structure, a fabric, an article of clothing, a building component, a building, and combinations thereof.

15. Use of a hydrated hydrogel having a lower critical solution temperature lower than 70 °C and which comprises at least one of a biocide or an algacide entrapped within the hydrated hydrogel in removing heat energy from an object.