

Description

Title of Invention: Composite particles comprising phase change materials

Technical Field

The present invention generally relates to composite particles comprising phase change materials. The present invention also relates to a method of preparing the same.

Background Art

Countries with heavy traffic and high building densities face critical energy and environmental issues. The building and construction industry is a prime consumer of the world's material and energy resources which accounts for nearly 40% of usage. Conventional use of fossil energy produces harmful emissions which cause environmental pollution. In an effort to promote smart living and conserve energy, various green technologies such as self-cleaning glass, solar-control glass and reflective paint are being developed. Among these technologies, thermal energy storage systems (TES) are considered a simple and effective solution to energy conservation. Sensible heat storage materials like steel, masonry and water, where thermal energy is stored by raising the temperature of the material, are widely used as TES materials in the building industry. Latent storage materials are however preferred because they provide more effective storage of heat with comparatively smaller amounts of material. Latent heat storage materials are referred to as phase change materials (PCMs), and generally refer to materials capable of undergoing solid-liquid phase change when subjected to changing temperatures. Phase-

change materials (PCMs) typically have a high heat of fusion and are capable of storing and releasing large amounts of energy. Integration of PCM into building materials can increase the thermal storage capacity and thermal insulation of the building envelope.

Indeed, PCMs have been tested and shown to be effective thermal storage/insulation components in buildings. PCMs can be categorized into three main classes, organic, inorganic and eutectics. Inorganic materials include salt hydrates and metallics. These compounds have a high latent heat per unit mass, non-flammable and comparatively low in cost. A eutectic is a combination of two or more components where each material melts and freezes congruently. Organic materials include paraffin and non-paraffins. They show good physical and chemical stability, good thermal behaviour, low super-cooling, good compatibility with construction materials. However, paraffin is flammable and has low thermal conductivity and may exhibit undesirably large volume changes when undergoing phase change.

Currently, organic PCMs have become quite attractive due to their advantages over inorganic materials. The drawbacks of inorganic PCMs include phase segregation and super cooling which affect their latent heat properties. Some unsuitable characteristics of the inorganic PCMs, such as very high volume change and supercooling during solid–liquid transition, have led to the hydrated salts not being considered as an appropriate material to be incorporated into concrete. Another disadvantage of inorganic PCMs is that they are prone to degradation and become inoperative after repeated phase change cycles. On the other hand, organic PCMs experience little super cooling and phase segregation and are generally compatible with various building materials. However, many organic

PCMs such as paraffin wax are flammable and possess low thermal conductivity and low enthalpy in its solid state.

Additionally, organic PCMs are typically incorporated into concrete via methods like simple immersion of the porous concrete in the melted (liquid) PCMs and vacuum impregnation of the PCMs in porous aggregates. However, such methods tend to lead to the loss of the PCM due to leakage from the concrete. Additionally, the incorporated PCM may lack durability and/or resistance to high heat or flame.

To address these issues, microencapsulated PCMs have been proposed for application to cement directly. The microencapsulated PCM show good compatibility with cement and possess improved durability. However, the low thermal conductivity of these PCMs remains a problem. In particular, the low thermal conductivity of the shell of PCMs inhibits the thermal energy transfer and reduces heat removal/absorption capability.

Accordingly, there is a need to provide a phase change material that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary of Invention

In one aspect, there is provided a composite particle comprising a core and a polymeric shell encapsulating the core, wherein the core comprises at least one organic phase change material and at least one thermally conductive material is dispersed within said polymeric shell.

Advantageously, the composite particle may be used as an additive to provide heat capacity to a material including, but not limited to, a building material e.g., cement. The

composite particle avoids the various disadvantages of inorganic PCM such as relatively larger change of volume during phase changes and relatively short life time (may become inactive after multiple cycles). The composite particle further provides improved thermal conductivity relative to conventional organic phase change materials which may not contain said thermally conductive material. Surprisingly, it has also been found that building materials added with the disclosed composite particles may outperform (in terms of thermal conductivity and/or heat capacity and/or durability of such properties) building materials having PCMs and thermally conductive additives added separately.

Advantageously, it is observed that the phase change material may remain contained within the polymeric shell even when the phase change material undergoes phase changes. The polymeric shell advantageously provides a barrier to prevent the phase change material from undesirable chemical or physical interactions with external components. The thermally conductive material advantageously increases the thermal conductivity of the disclosed composite particle, thereby enhancing the rate of absorbing/releasing thermal energy. The composite particle may therefore be used even in applications where the external components may potentially be reactive with the phase change material.

Furthermore, the encapsulation of the phase change material may prevent or reduce loss of phase change material during phase change, e.g., as volatile emissions or by being entrained in solvents e.g., water, rain, etc. This advantageously improves the total number of cycles of state changes that the composite material may provide, i.e., improved life-time.

Advantageously, it has been found that the composite particle may be resistant to thermal degradation or may be thermally stable up to a temperature of about 150°C, about 160°C, about 170°C, about 180°C, about 190°C, about 200°C, about 210°C, about 220°C, about 230°C, about 240°C, or about 250°C.

Another aspect relates to a method of preparing a composite particle comprising an organic phase change material core and a polymeric shell encapsulating the core, the method comprising: polymerizing at least one monomer compound in an oil-in-water emulsion, said oil-in-water emulsion comprising at least one organic phase change material and a surfactant, wherein said polymerization is undertaken in the presence of at least one thermally conductive material dispersed within said oil-in-water emulsion.

Definitions

The following words and terms used herein shall have the meaning indicated:

The expression “phase-change materials” or “PCMs” as used herein refers to substances with a high heat of fusion, undergo a phase change at a certain temperature, and are capable of storing and releasing large amounts of energy. The phase change may be, but not limited to, melting and solidifying. PCMs as disclosed herein may be organic, inorganic and eutectics compounds.

As used herein, the expression “cementitious material” refers to compositions comprising cement, which may include hydraulic or non-hydraulic cement. Such compositions may further comprise silica, sand, water, etc.

The expression “nano-particulates”, “nano-sized particles” or “nanoparticles” as used herein may refer to solid particles having at least one dimension selected from length, diameter, width and thickness, of less than 1000 nm.

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 invention.

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 elements.

As used herein, the term “about”, in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6

etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments 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.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a composite particle comprising a core and a polymeric shell encapsulating the core will now be disclosed.

The core of the composite particle may comprise at least one organic phase change material, wherein the organic phase change material is selected from the group consisting of paraffins, polyethylene glycols, fatty acids, polyalcohols, triglycerides, vegetable oils and mixtures thereof. Organic phase change materials are advantageously more chemically stable than their inorganic counterparts. Therefore, the disclosed composite particle may be used in applications involving a wider range of temperatures.

The organic phase change material may be selected from straight chain or branched hydrocarbons comprising about 100, or 95, or 90, or 85, or 80, or 75, or 70, or 65, or 60, or 55, or 50, or 45, or 40, or 35, or 30, or 25, or 20, or 15, or 14, or 13, or 12, or 11, or 10 carbon atoms, or less.

The organic phase change material may comprise octadecane and may be composed essentially of octadecane.

The polymeric shell of the composite particle may comprise one or more polymers selected from the group consisting of natural polymers, synthetic polymers and blends thereof. Where a natural polymer is to be used, it may be selected from the group consisting of lignin, fibrin, polysaccharides, agarose, cellulose sulfate, chondroitin sulfate, chitin, chitosan and hyaluronan.

Where a synthetic polymer is provided as the polymeric shell, the synthetic polymer may be prepared by polymerizing one or more monomer compounds selected from the group consisting of styrene, divinylbenzene, formaldehyde, phosphazenes, acrylic acid, methacrylic acid, alkylene oxides, vinyl acetate, vinylpyrrolidone, ethylene glycol and ethersulfone. In one embodiment, the synthetic polymer is polystyrene.

Advantageously, the polymeric shell may be resistant to thermal degradation or may be thermally stable up to a temperature of about 300°C, about 310°C, about 320°C, about 330°C, about 340°C, about 350°C, about 360°C, about 370°C, about 380°C, about 390°C, about 400°C, about 410°C, about 420°C, about 430°C, about 440°C, about 450°C, about 460°C, about 470°C, about 480°C, about 490°C, or about 500°C.

The core of the composite particle may comprise a thermally conductive material, wherein the thermally conductive material comprises nano-sized particles. The composite particle may comprise a polymeric shell. The composite particle may comprise a substantially hollow core. Within the core, a plurality of nano-sized

metal particles in admixture with solid particles of an organic phase change material may be encapsulated by the polymeric shell. The organic phase change material may be in the solid state or liquid state under room temperature condition, e.g. at about 20 °C, 25 °C, 30 °C, 35 °C and 40 °C. This depends on the melting temperature (T_M) of the phase change material used. The phase change material may have a T_M in the range of 15 °C to 45 °C, 20 °C to 40 °C, 25 °C to 35 °C, or 25 °C to 30 °C. In one embodiment, the PCM may have a T_M of around 28-30 °C. .

Advantageously, the surface area of nano-sized thermally conductive particulate material may be dramatically increased as compared to bulk thermally conductive material, thereby increasing rate and efficiency of thermal energy transfer.

The thermally conductive material may be a nano-particulate metal. The nano-particulate metal may be an element selected from Group 10, Group 11 or Group 12 of the Periodic Table of Elements. The element may be selected from the group consisting of nickel, platinum, copper, silver, gold, zinc and mixture thereof. Advantageously, nano-particulate metals may be 2-fold, 3-fold, 4-fold, 5-fold, 6-fold, or 7-fold more thermally conductive than bulk metals.

The thermally conductive material may have a thermal conductivity of at least about 1,000 W/mK, at least about 1,100 W/mK, at least about 1,200 W/mK, at least about 1,300 W/mK, at least about 1,400 W/mK, at least about 1,500 W/mK, at least about 1,600 W/mK, at least about 1,700 W/mK, at least about 1,800 W/mK, at least about 1,900 W/mK, at least about 2,000 W/mK, at least about 2,100 W/mK, at least about 2,200 W/mK, at least about 2,300 W/mK, at least about 2,400 W/mK, at least about 2,500 W/mK, at least about 2,600 W/mK, at least about 2,700 W/mK, at least about 2,800 W/mK or at least about 2,900 W/mK.

Where the disclosed thermally conductive material possesses the above range of thermal conductivities, the thermally conductive material may be included in the composite particle in small amounts to achieve a rate of thermal energy transfer comparable to non-encapsulated phase change materials, or compositions comprising encapsulated phase change materials mixed with conventional additives to enhance thermal conductivity. Advantageously, the use of a small amount of the thermally conductive material can enhance the thermal conductivity of the composite particle without the thermally conductive material by about 20%, 30%, 40%, 50% or 60%.

The thermally conductive material may be present in an amount of about 0.02 wt%, 0.03 wt%, 0.04 wt%, 0.05 wt%, 0.06 wt%, 0.07 wt%, 0.08 wt%, 0.09 wt%, 0.1 wt%, 0.11 wt%, 0.12 wt%, 0.13 wt%, 0.14 wt%, 0.15 wt%, 0.16 wt%, 0.17 wt%, 0.18 wt%, 0.19 wt%, or 0.2 wt% of the composite particle, or may be in a range comprising an upper limit and a lower limit selected from any two of the above.

Advantageously, it has been demonstrated that the addition of a small amount (0.02 wt.%) in the composite particle, may enhance the thermal conductivity of the composite particle by about 40%.

The polymeric shell may be present in an amount of about 40 wt%, 45 wt%, 50 wt%, 55 wt%, 60 wt%, 65 wt%, 70 wt%, 75 wt%, or 80 wt% of the composite particle, or is in a range comprising an upper limit and a lower limit selected from any two of the above.

The organic phase change material may be present in an amount of about 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 45 wt%, 50 wt%, 55 wt%, or 60 wt% of the composite particle, or in a range comprising an upper limit and a lower limit selected from any two of the above.

The weight percentage of each of said polymeric shell, said thermally conductive material and said organic phase change material may add up to 100%. The thermally conductive material may be copper, silver, or mixtures of both.

Where the thermally conductive material is nano-particulate copper, the thermal conductivity may be about 2,900 W/mK to about 3,000 W/mK, or about 2,971 W/mK. Where the thermally conductive material is nano-particulate silver, the thermal conductivity may be about 3,000 W/mK.

The thermally conductive material may be in the form of a wire, sphere, cylinder, or coin. The thermally conductive material may be surface treated to improve compatibility with the polymeric shell. The surface treatment may comprise functionalizing a surface of the thermally conductive material with one or more reactive functional groups. Such functional groups may include hydroxy, carbonyl, siloxane, silane, epoxy, alkoxysilane, or combinations thereof. In one embodiment, the thermally conductive material may be silanized prior to being added to the polymerization mixture for preparing the composite particle of the present disclosure.

The silanization may be performed by contacting a surface of the thermally conductive material with a silane source. The silane source may comprise organofunctional alkoxysilane, which may be selected from the group consisting of:

aminosilanes, glycidoxysilanes, mercaptosilanes and mixtures thereof. The silane source may be optionally pre-hydrolyzed to provide a plurality of silanol groups, which may undergo condensation to form siloxane (-Si-O-Si-) groups. Accordingly, the silane source may be dimerized, oligomerized or polymerized.

Exemplary aminosilanes may include (3-aminopropyl)-triethoxysilane, (3-aminopropyl)-diethoxy-methylsilane, (3-aminopropyl)-dimethyl-ethoxysilan, and (3-aminopropyl)-trimethoxysilane. Exemplary mercaptosilanes may include (3-mercaptopropyl)-trimethoxysilane and 3-mercaptopropyl)-methyl-dimethoxysilane. In one embodiment, the silane source may be (3-mercaptopropyl)trimethoxysilane (MTPTS), hydrolyzed (3-mercaptopropyl)trimethoxysilane or a mixture thereof.

In one embodiment, the surface treatment may involve mixing the thermally conductive material with the silane source in water, an aqueous phase or a solvent selected from acetone, ethanol and isopropanol. In an embodiment, the mixing may be under continuous agitation for about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours and about 10 hours. The mixing may be carried out at room temperature. The thermally conductive material may then be centrifuged and filtered to obtain the surface-treated thermally conductive material. Advantageously, a composite nanoparticle comprising a shell with silanized thermally conductive material may form a stable dispersion in an organic solvent. The composite nanoparticle would otherwise form unstable suspension in an organic solvent without the silanized thermally conductive material. Further advantageously, the enhanced dispersibility of composite nanoparticles having silanized shell in organic solvents may allow a coating of a composition comprising the composite nanoparticles to be applied onto surfaces more easily and uniformly

In one embodiment, the thermally conductive material may be copper nanowires. The copper nanowires may be surface treated by mixing with the silane and a solvent. The copper nanowires may be mixed with MTPTS, hydrolysed MTPTS or a mixture thereof. Additionally, the copper nanowires may also be mixed with acetone, ethanol or isopropanol. In an embodiment, the copper nanowires may surface treated by mixing with the silane and water. A layer of silica coating or a silica shell may be formed on the copper nanowires, thereby partially or fully encapsulating the copper nanoparticles. After treatment, the copper nanowires may be fully or partially encapsulated by a silica coating (Cu@SiO_2) comprising thiol functional groups.

The nanowires may have a diameter selected from about 100 nm to 10 μm . The nanowires may have a diameter selected from about 0.1 nm, or 0.5 nm, or 1 nm, or 2 nm, or 5 nm, or 10 nm, or 15 nm, or 20 nm, or 25 nm, or 30 nm, or 35 nm, or 40 nm, or 45 nm, or 50 nm, or 55 nm, or 60 nm, or 65 nm, or 70 nm, or 75 nm, or 80 nm, or 85 nm, or 90 nm, or 95 nm, or 100 nm, or 110 nm, or 120 nm, or 130 nm, or 140 nm, or 150 nm, or 160 nm, or 170 nm, or 180 nm, or 190 nm, or 200 nm, or 220 nm, or 240 nm, or 260 nm, or 280 nm, or 300 nm, or 320 nm, or 340 nm, or 360 nm, or 380 nm, or 400 nm, or 420 nm, or 440 nm, or 460 nm, or 480 nm, or 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 1000 nm, 1500 nm, 2000 nm, 2500 nm, 3000 nm, 3500 nm, 4000 nm, 5000 nm, 6000 nm, 7000 nm, 8000 nm, 9000 nm, 10 μm , or may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The nanowires may have a length selected from about 100 nm to 500 μm . The length of the nanowires may be about 100 nm, 150 nm, 200 nm, 250 nm, 300 nm,

350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 1000 nm, 1500 nm, 2000 nm, 2500 nm, 3000 nm, 3500 nm, 4000 nm, 5000 nm, 6000 nm, 7000 nm, 8000 nm, 9000 nm, 10 μm , 20 μm , 30 μm , 40 μm , 50 μm , 60 μm , 70 μm , 80 μm , 90 μm , 100 μm , 150 μm , 200 μm , 250 μm , 300 μm , 350 μm , 400 μm , 450 μm , 500 μm , or may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The nanowire may have a length-to-diameter ratio selected from 5000:1 to 10:1. The length-to-diameter ratio may be about 5000:1, 4500:1, 4000:1, 3500:1, 3000:1, 2500:1, 2000:1, 1800:1, 1600:1, 1400:1, 1200:1, 1000:1, 950:1, 900:1, 850:1, 800:1, 750:1, 700:1, 650:1, 600:1, 550:1, 500:1, 450:1, 400:1, 350:1, 300:1, 250:1, 200:1, 150:1, 100:1, 50:1, 45:1, 40:1, 35:1, 30:1, 25:1, 20:1, 18:1, 16:1, 14:1, 12:1, 10:1, or may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The composite particle may have a diameter selected from about 20 μm to 100 μm . The composite particle may have a diameter selected from about 20 μm , or 25 μm , or 30 μm , or 35 μm , or 40 μm , or 45 μm , or 50 μm , or 55 μm , or 60 μm , or 65 μm , or 70 μm , or 75 μm , or 80 μm , or 85 μm , or 90 μm , or 95 μm , or 100 μm , or may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The composite particle may be prepared by polymerizing at least one monomer compound in an oil-in-water emulsion, said emulsion comprising at least one organic phase change material and a surfactant, wherein said polymerization may be undertaken in the presence of at least one thermally conductive material as defined herein, and wherein the thermally conductive material may be dispersed

within said oil-in-water emulsion. Advantageously, as a result of such polymerization, the thermally conductive material may be substantially dispersed throughout the polymer matrix of the polymeric shell. The thermally conductive material may also be encapsulated within the core of the composite particle in mixture with the organic PCM particles.

The present disclosure further relates to a method of preparing a composite particle comprising an organic phase change material core and a polymeric shell encapsulating the core, the method comprising: polymerizing at least one monomer compound in an oil-in-water emulsion, said emulsion comprising at least one organic phase change material and a surfactant, wherein said polymerization is undertaken in the presence of at least one thermally conductive material dispersed within said oil-in-water emulsion.

The organic phase change material may advantageously form oil droplets in an aqueous environment in the presence of a surfactant. The thermally conductive material may be advantageously dispersed throughout the oil-in-water emulsion and within the oil droplets. The at least one monomer compound may be hydrophilic and soluble in the continuous water phase. The organic phase change material may be hydrophobic and soluble in the oil phase. The thermally conductive material may be at least partially hydrophilic and may associate with the monomer compound in the continuous water phase. Advantageously, the at least one monomer compound may be capable of polymerizing or forming a polymer around the oil droplets to thereby encapsulate them. The surfactant may advantageously aid the polymer in forming a micelle around the organic phase change material. Due to the hydrophilicity, the thermally conductive material associates with the polymer micelle and is dispersed within and substantially

throughout the polymer micelle. The polymeric shell comprising the thermally conductive material dispersed therein is therefore formed around a core comprising the organic phase change material, thereby encapsulating the core.

Advantageously, the disclosed composite particle may be prepared via a one-pot polymerization process. The disclosed composite particle may be formed in situ. Accordingly, the disclosed method does not require complex reactions.

In the method as disclosed herein, the thermally conductive material may comprise nano-sized particles. In embodiments, the nano-sized particles are nano-sized metal particles, e.g., nanowires.

In the method disclosed herein, the thermally conductive material may be provided in an amount of about 0.02 wt%, 0.03 wt%, 0.04 wt%, 0.05 wt%, 0.06 wt%, 0.07 wt%, 0.08 wt%, 0.09 wt%, 0.1 wt%, 0.11 wt%, 0.12 wt%, 0.13 wt%, 0.14 wt%, 0.15 wt%, 0.16 wt%, 0.17 wt%, 0.18 wt%, 0.19 wt%, or 0.2 wt% of the composite particle, or wherein the amount may be in a range comprising an upper limit and a lower limit selected from any two of the above. In one embodiment, the thermally conductive material is provided in an amount from about 0.02 wt. % to 0.2 wt. % based on the weight of the composite particle.

Advantageously, the thermally conductive material may be in the form of nanostructures possessing increased thermal conductivity. A lower amount of the thermally conductive material may advantageously be required in the emulsion to achieve comparable thermal conductivity as providing thermally conductive material in bulk form.

In the disclosed method, the monomer compound may be provided in an amount of about 40 wt%, 45 wt%, 50 wt%, 55 wt%, 60 wt%, or 65 wt% based on the total weight of said monomer compound, said organic phase change material and said thermally conductive material, or wherein the amount may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The surfactant may be provided in an amount of about 10 wt%, 15 wt%, 20 wt%, or 25 wt% based on the total weight of the mixture comprising the monomer compound, the organic phase change material and the thermally conductive material. The amount of surfactant added may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The phase change material may be provided in an amount of about 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 45 wt%, 50 wt%, 55 wt%, or 60 wt% of the composite particle, or wherein the amount may be in a range comprising an upper limit and a lower limit selected from any two of the above.

The polymerization may be undertaken in the presence of a polymerization initiator. The polymerization may be undertaken at a temperature of about 80°C, 85°C, 90°C, 95°C, or 100°C, or is in a range comprising an upper limit and a lower limit selected from any two of the above. The polymerization may be undertaken for a duration of about 5 hours, 6 hours, or 7 hours, or is in a range comprising an upper limit and a lower limit selected from any two of the above.

Advantageously, the disclosed method may not require extreme reaction conditions and may be conducted without the use of specialized equipment. The method as disclosed herein, wherein the organic phase change material may be

selected from the group consisting of paraffins, polyethylene glycols, fatty acids, polyalcohols, polyethylenes and mixtures thereof.

The organic phase change material may be selected from straight chain or branched hydrocarbons comprising about 100, or 95, or 90, or 85, or 80, or 75, or 70, or 65, or 60, or 55, or 50, or 45, or 40, or 35, or 30, or 25, or 20 carbon atoms, or less. The organic PCM may comprise from about 10-30 carbon atoms, 10-25 carbon atoms, 10-20 carbon atoms, 10-18 carbon atoms or 10-15 carbon atoms. The organic PCM may be selected from paraffins, polyethylene glycols, fatty acids, polyalcohol, triglycerides, vegetable oils and a mixture thereof. In one embodiment, the organic phase change material comprises or consists essentially of octadecane.

The polymeric shell may comprise one or more polymers selected from the group consisting of natural polymers, synthetic polymers and blends thereof.

The at least one monomer compound may be selected from the group consisting of styrene, divinylbenzene, formaldehyde, phosphazenes, acrylic acid, methacrylic acid, alkylene oxides, vinyl acetate, vinylpyrrolidone, ethylene glycol and ethersulfone. In one embodiment, the monomer used is styrene for preparing a polystyrene polymeric shell.

Where a natural polymer is to be used, it may be selected from the group consisting of alginate, collagen, gelatin, fibrin, polysaccharides, agarose, cellulose sulfate, chondroitin, sulfate, chitosan and hyaluronan.

The thermally conductive material used in the method may be one as described herein. Such materials may be selected for their thermal conductivity property. For instance, materials having a thermal conductivity of at least about 1,000 W/mK, at least about 1,100 W/mK, at least about 1,200 W/mK, at least about 1,300 W/mK, at least about 1,400 W/mK, at least about 1,500 W/mK, at least about 1,600 W/mK, at least about 1,700 W/mK, at least about 1,800 W/mK, at least about 1,900 W/mK, at least about 2,000 W/mK, at least about 2,100 W/mK, at least about 2,200 W/mK, at least about 2,300 W/mK, at least about 2,400 W/mK, at least about 2,500 W/mK, at least about 2,600 W/mK, at least about 2,700 W/mK, or at least about 2,800 W/mK may be preferably selected.

In embodiments of the disclosed method, copper nanowires are provided together with an organic PCM (e.g., octadecane) in the polymerizing mixture for encapsulation in a composite particle as described herein.

In an embodiment, the present disclosure provides a composite particle comprising a core and a polymeric shell encapsulating the core, wherein the core comprises at least one organic phase change material and at least one thermally conductive material in admixture with said phase change material, wherein the composite particle is produced by oil-in-water emulsion polymerization.

In an embodiment, there is provided a building material comprising the composite particle as disclosed herein. The building material as disclosed herein may further comprise cement. The building material may comprise at least about 10 wt%, or at least about 15 wt%, or at least about 20 wt%, or at least about 25 wt%, or at least about 30 wt%, or at least about 35 wt%, or at least about 40 wt%, or at least about 45 wt%, or at least about 50 wt%, or at least about 55 wt%, or at least about 60

wt%, or at least about 65 wt%, or at least about 70 wt%, or at least about 75 wt%, or at least about 80 wt% of the composite particle.

In an embodiment, there is provided a cementitious material comprising the composite particle as disclosed herein. The composite particle may comprise at least about 10 wt%, or at least about 15 wt%, or at least about 20 wt%, or at least about 25 wt%, or at least about 30 wt%, or at least about 35 wt%, or at least about 40 wt%, or at least about 45 wt%, or at least about 50 wt%, or at least about 55 wt%, or at least about 60 wt%, or at least about 65 wt%, or at least about 70 wt%, or at least about 75 wt%, or at least about 80 wt% of the cementitious material.

Advantageously, the disclosed composite particle may not be chemically reactive with the building material and/or the cementitious material. The disclosed composite particle may be compatible with the building material and/or the cementitious material. The function of the building material or the cementitious material may not be undesirably affected by the incorporation of the composite particle.

Advantageously, the phase change material encapsulated within the composite particle can increase the specific heat capacity of the building material and/or the cementitious material. Thus, the disclosed building material and/or the cementitious material are capable of storing and releasing increased amounts of thermal energy.

Advantageously, the thermally conductive material encapsulated within the composite particle increases the heat transfer coefficient of the composite particle. Thermal energy is therefore advantageously transferred to and from the phase

change material encapsulated within the composite particle with the aid of the thermally conductive material also encapsulated within the composite particle. The transfer loss of thermal energy to other components of the building material and/or the cementitious material or to the surroundings may therefore be reduced.

Accordingly, the disclosed building material and/or cementitious material may enable thermal energy transfer to be targeted, i.e., thermal energy is absorbed or removed from the composite particle, as compared to a composition comprising phase change material and additives added separately and not encapsulated within the phase change material.

Advantageously, the building material and/or the cementitious material may be resistant to thermal degradation or may be thermally stable up to a temperature of about 600°C, about 610°C, about 620°C, about 630°C, about 640°C, about 650°C, about 660°C, about 670°C, about 680°C, about 690°C, about 700°C, about 710°C, about 720°C, about 730°C, about 740°C, about 750°C, about 760°C, about 770°C, about 780°C, about 790°C, or about 800°C.

Advantageously, the building material and/or the cementitious material may possess a specific heat capacity of about 15 J/g·°C, about 20 J/g·°C, about 25 J/g·°C, about 30 J/g·°C, about 35 J/g·°C, about 40 J/g·°C, about 45 J/g·°C, about 50 J/g·°C, about 55 J/g·°C, about 60 J/g·°C, about 65 J/g·°C, about 70 J/g·°C, or is in a range comprising an upper limit and a lower limit selected from any two of the above.

The specific heat capacity of the disclosed building material and/or cementitious material may be more than about 1000%, or more than about 1500%, or more than

about 2000%, or more than about 2500%, or more than about 3000%, or more than about 3500%, or more than about 4000%, or more than about 4500%, or more than about 5000%, or more than about 5500%, or more than about 6000%, or more than about 6500%, or more than about 7000%, or more than about 7500%, or more than about 8000%, or more than about 8500%, or more than about 9000%, or more than about 9500%, or more than about 10000%, or more than about 10500%, or more than about 11000%, or more than about 11500%, or more than about 12000%, than that of building and cementitious material that do not comprise the disclosed composite particle.

Brief Description of Drawings

The accompanying drawings illustrate one or more disclosed embodiments and serves to explain the principles of the present invention. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

[Fig. 1] contains Scanning Electron Microscopy (SEM) images showing the morphology of microencapsulated PCMs at (a) low magnification and at (b) high magnification.

Fig. 2

[Fig. 2] is a Thermogravimetric Analysis (TGA) graph comparing the thermal stability between a pure cement sample, a cement sample doped with 25% PCM

according to the present invention (w/w, 3/1) and another cement sample doped with 50% PCM according to the present invention (w/w, 1/1).

Fig. 3

[Fig. 3] is a Differential Scanning Calorimetry (DSC) graph demonstrating the difference in the heat capacities of the pure cement sample, the cement/PCM (w/w, 3/1) sample and the cement/PCM (w/w, 1/1) sample.

Fig. 4

[Fig. 4] shows the Heat Chamber test setup with IR lamp for (a) pure cement sample (left) and cement/PCM (3/1) sample (right); and (b) pure cement sample (left) and cement/PCM (1/1) sample (right). The intensity of the IR radiation was adjusted to achieve consistent top surface temperature at about 80 °C for all the test samples.

Fig. 5

[Fig. 5] shows a plot of testing temperature of the IR lamp and the temperature difference between cement and cementitious materials containing PCMs. The ■ data plot indicates the temperature difference between the pure cement sample and the cement/PCM (w/w, 3/1) sample; the ● data plot indicates the temperature difference between the pure cement sample and the cement/PCM (w/w, 1/1) sample.

Fig. 6

[Fig. 6] shows the Heat Chamber test setup with IR lamp for (a) pure cement sample (left) and cement/PCM (3/1) sample with copper nanowires (right); and (b)

pure cement sample (left) and cement/PCM (3/1) sample without copper nanowires (right). The intensity of the IR radiation was adjusted to achieve consistent top surface temperature at about 80 °C for all the test samples.

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.

Example 1 – Preparation of microencapsulated PCMs comprising copper nanowires

The microencapsulated PCMs comprising copper nanowires were synthesized via simple in-situ polymerization procedures. First, 150 ml Deionized (DI) water was added into 250 ml three-necked RBF under rigorous stirring and argon protection. Second, 1.5 g polyvinylpyrrolidone (PVP) power was added as a surfactant. The mixture was maintained at 28 °C for 30 mins until all the PVP were dissolved. Next, 7 ml octadecane was added and the reaction mixture was stirred for another 30 mins. Thereafter, 1.4 g copper nanowires were added into the mixture.

The copper nanowires were surface treated prior to use. 500 mL of (3-Mercaptopropyl)trimethoxysilane (MPTMS, purchased from Sigma-Aldrich) was added to 200 mL of deionized water to afford a turbid solution. At room temperature, the resulting solution was shaken at 300 rpm for 1 hour until a transparent solution was obtained, indicating that MPTMS has been partially hydrolyzed. 30 mL of the pre-hydrolyzed MPTMS aqueous solution was then mixed with 1g Cu NPs to form a clear solution for silica coating. The resulting solution was continuously shaken at 500 rpm for about 6 hours, followed by centrifugation

at 3000 rpm for 10 minutes to recover Cu@SiO₂-SH NPs. The core-shell Cu@SiO₂-SH NPs were purified by washing with deionized water via redispersion–centrifugation cycle for at least three rounds. The obtained Cu@SiO₂-SH NPs (or encapsulated Cu) were redispersed in 10 mL of deionized water for further use.

Once a uniform solution mixture was obtained, 8.3 ml styrene monomers were added into mixture, which is stirred for another 30 mins. Next, the temperature was increased to 90 °C with the addition of 0.35 g benzoyl peroxide (BPO) as the polymerization initiator. The mixture was refluxed for 6 hours. Finally, the reaction was cooled to room temperature. The mixture was filtrated via the filter paper. The precipitates were then collected and dried. The resultant dried precipitates are the high-performance microencapsulated PCMs with copper nanowires.

The morphology of microencapsulated PCMs doped with copper nanowires are shown in Fig. 1. Fig. 1 (b) clearly shows the uniform PCM shells obtained from the method above. Further, the dark hole in the PCM shells, as can be seen from Fig. 1(a), shows that these micro-sized spheres are hollow, which contains PCMs and copper nanowires.

Example 2 – Thermal analysis of microencapsulated PCMs comprising copper nanowires

In order to validate the suitability of the microencapsulated PCMs for use in concrete for smart concrete and building efficiency, thermal analysis was conducted on the various batches of panels containing different concentration of microencapsulated PCMs comprising copper nanowires to examine the thermal insulation properties and the heat capacity of the panels. The cement panels that

were tested are: cement [0% PCMs], cement/PCM (w/w, 3/1) [25% PCMs] and cement/PCM (w/w, 1/1) [50% PCMs]. To eliminate the effects of volume and weight of the test panels on the thermal analysis, the test panels were fabricated in uniform size of 30 cm × 30 cm × 1 cm and weight of 400 g.

In order to examine the thermal stability for those cementitious materials containing PCMs, thermogravimetric analyses (TGA) were carried out with a heating rate of 20 °C/min from ambient temperature up to 900 °C in air. As shown in Fig. 2, all these samples show good thermal stability up to 200 °C, which fully satisfy the requirement for applications as normal building materials. Compared to pure cement, cementitious materials containing PCMs exhibit another two degradation steps. The first degradation step is mostly attributed to the reaction of octadecane. The second step between 350-400 °C is likely to result from the degradation of polystyrene, which matches well with thermal behaviour of pure polystyrene. When the temperature goes beyond the 700 °C, a significant weight decrease can be found for all three samples, which may be attributed to the reaction of materials in cement.

In addition to the TGA test, Differential Scanning Calorimetry (DSC) analyses were also conducted to evaluate the heat capacity of cementitious materials which is an important property in controlling the stable temperature of a building. DSC was run from 0 to 70 °C with a cooling rate of 10 °C/min and a heating rate of 5 °C/min. As shown in Fig. 3, with the incorporation of microencapsulated PCMs, the cementitious materials containing PCMs all exhibit significantly higher heat capacity in comparison with pure cement. Table 1 summarises the DSC data for the tested cement panels. The heat capacities for cement, cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1) are 0.3679, 19.34 and 41.36 J/g, respectively.

Therefore, compared with pure cement, heat capacities for cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1) are increased by 5156% and 11142%, respectively.

Table 1 DSC data for cement, cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1).

Samples	Heat Capacity Peak (°C)	Heat Capacity (J/g)
Cement	26.69 °C	0.3679 J/g
Cement/PCM (3/1)	26.94 °C	19.34 J/g
Cement/PCM (1/1)	26.89 °C	41.36 J/g

Furthermore, Table 2 shows the heats flux test for three samples with the same thickness of 1 cm while Table 3 shows the heats flux test for three cement samples with the same weight.

Table 2 Heat flux test for cement, cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1) samples with same thickness.

Samples	Conductivity (W/mk)	Resistivity (m ² K/W)	Upper (°C)	Lower (°C)
Cement	0.39	2.56×10^{-2}	41.15	16.44
Cement/PCM (3/1)	0.24	4.02×10^{-2}	42.69	13.39
Cement/PCM (1/1)	0.20	5×10^{-2}	43.51	11.87

Table 3 Heat flux test for cement, cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1) samples with same weight.

Samples	Conductivity (W/mk)	Resistivity (m ² K/W)	Upper (°C)	Lower (°C)
Cement	0.31	3.1×10^{-2}	41.64	13.53
Cement/PCM (3/1)	0.28	4.29×10^{-2}	42.90	13.11
Cement/PCM (1/1)	0.27	5.5×10^{-2}	43.32	12.83

For the same thickness, all samples were made to a disc with 5 cm diameter and 1 cm thickness. As demonstrated by the results in Table 2, an increase in the PCM content leads to lower thermal conductivity, implying an improvement to the insulating property of the cement. Further, the thermal conductivity of cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1) is 38% and 48% lower than that of pure cement. Similarly, the thermal resistivity increases with an increase in the PCM content. As shown in Table 3, thermal conductivity for samples with same weight was also examined. With an increase in PCM content, the thermal conductivity reduces, resulting in enhanced insulating property.

Hence, the addition of microencapsulated PCMs, advantageously, greatly enhances the thermal insulation of cement panels and can advantageously be used in cement materials to optimize the temperature of buildings.

The cement samples were subjected to further tests in heat chamber with IR lamp as shown in Fig. 4. Temperature difference between cement and cementitious materials containing PCMs at different testing temperatures (Entries 1, 2 and 3 in ascending order of IR intensities) were performed and the results are displayed in Table 4 and Fig. 5. When the IR lamp was switched on, the top surface of the samples received the heat emitted from the IR lamp. The heat would then be conducted to the bottom surface of the samples. The resultant temperature at the bottom surface is an indication of the heat capacity and the insulation effect of the sample. Compared to pure cement panel, panels with PCM exhibit more effective temperature reduction. As can be seen from Table 4, the temperature reduction could be as high as 12.5 °C for cement/PCM (1/1). Higher content of PCM leads to better passive cooling. Therefore, advantageously, cementitious materials

containing PCMs exhibit excellent performance in controlling the temperature due to their good heat capacity and heat insulation.

Table 4 Heat reduction test for cement, cement/PCM (w/w, 3/1) and cement/PCM (w/w, 1/1).

Entry	Cement (°C)	Cement/PCM (3/1) (°C)	ΔT (°C)	Cement (°C)	Cement/PCM (1/1) (°C)	ΔT (°C)
1 Top surface	60.3	60.4	5.6	60.5	60.2	5.7
1 Bottom surface	29.5	23.9		29.1	23.4	
2 Top surface	70.6	70.5	7.4	70.5	70.1	8.7
2 Bottom surface	31.8	24.4		31.7	23.5	
3 Top surface	80.5	80.0	10.8	80.2	80.4	12.5
3 Bottom surface	37.2	26.4		36.9	24.4	

Further, to study the effect of the presence of copper nanowires in the PCM, samples of cement/PCM (3/1) with and without copper nanowires were subjected to the heat chamber with IR lamp test as described above. As shown in Fig. 6(a), the temperature difference between the top and bottom surfaces of the pure cement sample (left) is 43.3 °C and that of the cement/PCM (3/1) sample with copper nanowires (right) is 53.6 °C. The improvement in heat reduction is 10.3 °C. In comparison, Fig. 6(b) shows that the temperature difference between the top and bottom surfaces of the pure cement sample (left) is 48.8 °C and that of the cement/PCM (3/1) sample without copper nanowires (right) is 56 °C. When copper nanowires are not present, the enhancement in heat reduction is only 7.2 °C. It is clear from this study that the cement/PCM sample without copper nanowires leads to less temperature reduction. This may be due to incomplete melting of PCM as a result of poor heat conductivity to the PCM. Conversely, when copper nanowires are present, the heat conductivity to the PCM core of the composite nanoparticles

is advantageously enhanced, leading to more heat being transferred to the PCM than through the cement panel.

Industrial Applicability

The potential industrial applications of the disclosed composite particle and the method of preparation thereof are self-evident. The disclosed composite particle could be integrated into materials for increasing the thermal storage capacity and the thermal insulation of the materials. The disclosed composite particle could also be incorporated into cementitious materials or compositions to advantageously provide higher heat capacity and enhanced thermal insulation to a building constructed using the materials or compositions. The disclosed method of the present application is simple and could produce the disclosed composite particle at low-cost.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A composite particle comprising a core and a polymeric shell encapsulating the core, wherein the core comprises at least one organic phase change material and wherein the shell comprises at least one thermally conductive material in an amount of from 0.02 wt. % to 0.2 wt. % of the composite particle; and wherein the thermally conductive material comprises nano-sized metal particles selected from copper nanoparticles, silver nanoparticles, or mixtures of both.
2. The particle of claim 1, wherein the organic phase change material is selected from the group consisting of paraffins, polyethylene glycols, fatty acids, polyalcohols, triglycerides, vegetable oils and mixtures thereof.
3. The particle of claim 1, wherein the organic phase change material is selected from straight chain or branched hydrocarbons comprising from 10 to 100 carbon atoms.
4. The particle of claim 3, wherein the organic phase change material comprises octadecane.
5. The particle of any one of claims 1 to 4, wherein the polymeric shell comprises a polymer formed from one or more monomer compounds selected from the group consisting of styrene, divinylbenzene, formaldehyde, phosphazenes, acrylic acid, methacrylic acid, alkylene oxides, vinyl acetate, vinylpyrrolidone, ethylene glycol and ethersulfone.

6. The particle of any one of claims 1 to 4, wherein the polymeric shell comprises a natural polymer selected from the group consisting of lignin, fibrin, polysaccharides, agarose, cellulose sulfate, chondroitin sulfate, chitin, chitosan and hyaluronan.
7. The particle of any one of the preceding claims, wherein the thermally conductive material comprises nanowires having a length of 100 μm to 500 μm and a diameter of 100 nm to 10 μm .
8. The particle of any one of the preceding claims, wherein the at least one thermally conductive material comprises a surface that has been functionalized with reactive functional groups selected from the group consisting of: hydroxyl, carbonyl, silanol, silane, epoxy and combinations thereof.
9. The particle of any one of the preceding claims, wherein the at least one thermally conductive material comprises a silanol-functionalized surface or a silane-functionalized surface.
10. The particle of any one of the preceding claims, comprising
 - the polymeric shell in an amount of from 40 wt. % to 80 wt. % of the composite particle;
 - the organic phase change material in an amount of from 20 wt% to 60 wt. % of the composite particle; and
 - wherein the total wt. % is 100%.

11. The particle of any one of the preceding claims, having a diameter selected from 20 μm to 100 μm .

12. A method of preparing a composite particle comprising an organic phase change material core and a polymeric shell encapsulating the core, the method comprising:

polymerizing at least one monomer compound in an oil-in-water emulsion, said oil-in-water emulsion comprising at least one organic phase change material and a surfactant,

wherein said polymerization is undertaken in the presence of at least one thermally conductive material dispersed within said oil-in-water emulsion;

wherein the thermally conductive material is provided in an amount of from 0.02 wt% to 0.2 wt% of the composite particle; and

wherein the thermally conductive material comprises nano-sized metal particles selected from copper nanoparticles, silver nanoparticles, or mixtures of both.

13. The method of claim 12, wherein the at least one thermally conductive material is surface treated prior to the polymerization step; and wherein said surface treatment functionalizes the thermally conductive material with one or more functional groups consisting of: hydroxyl, carbonyl, silanol, silane, epoxy and combinations thereof.

14. The method of claim 13, wherein the at least one thermally conductive material is surface treated with a silane source to partially or fully encapsulate the thermally conductive material within a silica shell.

15. The method of any one of claims 12-14, wherein the monomer compound is provided in an amount of from 40 wt% to 80 wt.% based on the total weight of said monomer compound, said organic phase change material and said thermally conductive material;

the surfactant is provided in an amount of from 10 wt% to 25 wt% based on the total weight of said monomer compound, said organic phase change material and said thermally conductive material; and wherein

the phase change material is provided in an amount of from 20 wt.% to 60 wt. % of the composite particle.

16. The method of any one of claims 12-15, wherein the organic phase change material is selected from straight chain or branched hydrocarbons comprising from 10 to 100 carbon atoms.

17. The method of claim 16, wherein the organic phase change material comprises octadecane.

18. The method of any one of claims 12-17, wherein the at least one monomer compound is selected from the group consisting of styrene, divinylbenzene, formaldehyde, phosphazenes, acrylic acid, methacrylic acid, alkylene oxides, vinyl acetate, vinylpyrrolidone, ethylene glycol and ethersulfone.

19. The method of any one of claims 12-18, wherein the thermally conductive material comprises nanowires having a having a length of 100 μm to 500 μm and a diameter of 100 nm to 10 μm .

20. A building material comprising a cementitious material and the composite particle of any one of claims 1-11.

21. The building material of claim 20, comprising from 10 to 75 wt. % of said composite particles.