CELLULOSIC COMPOSITE MATERIALS AND METHODS THEREOF

CROSS-REFERENCE

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 62/995,877, filed February 18, 2020, and U.S. Provisional Patent Application Serial No. 63/088,644, filed October 7, 2020, each of which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Cellulosic materials can be used as building insulation materials. The cellulosic materials can be broken down into pieces and inserted into (e.g., blown in) cavities of roofs, walls, or floors, e.g., to provide thermal and acoustic insulation.

SUMMARY

[0002a] In an aspect of the present disclosure, there is provided a composite material, comprising:

a cellulosic material characterized by one or more members selected from the group consisting of (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores; and

a binder material comprising lime, wherein the lime comprises calcium oxide or calcium hydroxide.

[0002b] In another aspect of the present disclosure, there is provided a method for generating a composite material, comprising

(a) providing (1) a cellulosic material characterized by one or more members selected from the group consisting of: (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores and (2) a binder material comprising lime, wherein the lime comprises calcium oxide or calcium hydroxide; and

(b) mixing the cellulosic material and the binder material, to generate the composite material.

[0003] An ~~aspect~~example of the present disclosure provides a composite material, comprising: a cellulosic material characterized by one or more members selected from the group consisting of (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores; and a binder material comprising lime, wherein the lime comprises calcium oxide or calcium hydroxide.

[0004] In some ~~embodiment~~examples, the lime comprises calcium oxide and calcium hydroxide.

[0005] In some ~~embodiment~~examples of any one of the subject composite materials, the binder material further comprises silica. In some ~~embodiment~~examples of any one of the subject composite materials, a weight ratio of the silica (S) and the lime (L) is between about 1:1 and about 1:5 (S:L). In some ~~embodiment~~examples of any one of the subject composite materials, a weight ratio of the silica (S) and the lime (L) is about 1:3 (S:L).

[0006] In some ~~embodiment~~examples of any one of the subject composite materials, a weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 1:10 and about 20:10 (BM:CM). In some ~~embodiment~~examples, the weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 7:10 and about 15:10 (BM:CM). In some ~~embodiment~~examples, the weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 1:10 and about 2:10.

[0007] In some ~~embodiment~~examples of any one of the subject composite materials, the binder material further comprises silicate. In some ~~embodiment~~examples, the silicate comprises silicate nanocrystals or silicate microcrystals. In some ~~embodiment~~examples, the silicate comprises calcium silicate hydrate (C-S-H) nanocrystals or C-S-H microcrystals.

[0008] In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material comprises one or more members selected from the group consisting of: a bast fiber, leaf, seed, fruit, grass, and wood. In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material comprises a hemp bast fiber.

[0009] In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material comprises hemp long bast fiber or short hurd fiber. In some ~~embodiment~~examples, the cellulosic material comprises the hemp long bast fiber and the short hurd fiber

[0010] In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material characterized by two or more members selected from the group consisting of (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores. In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material characterized by (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores.

[0011] In some ~~embodiment~~examples of any one of the subject composite materials, the composite material is characterized by having a density between about 1 pounds per cubic foot (lb/ft^3) and about 100 lbs/ft^3. In some ~~embodiment~~examples of any one of the subject composite materials, the composite material is characterized by having a density between about 1 lb/ft^3 and about 30 lbs/ft^3. In some ~~embodiment~~examples of any one of the subject composite materials, the composite material has a density between about 5 lb/ft^3 and 25 lb/ft^3. In some ~~embodiment~~examples of any one of the subject composite materials, the composite material is characterized by having a density of at least about 5 lbs/ft^3.

[0012] In some ~~embodiment~~examples of any one of the subject composite materials, the composite material is usable as a thermal or acoustic insulator for a building.

[0013] In some ~~embodiment~~examples of any one of the subject composite materials, the composite material exhibits a biocidal activity against a microorganism.

[0014] In some ~~embodiment~~examples of any one of the subject composite materials, the cellulosic material exhibits enhanced shelf-life as compared to a cellulosic material that does not exhibit the characterization.

[0015] Another ~~aspect~~example of the present disclosure provides a method for generating a composite material, comprising: (a) providing (1) a cellulosic material characterized by one or more members selected from the group consisting of: (i) at least a portion of the cellulosic material is delignified, (ii) at least a portion of crystal structure of the cellulosic material is maintained, and (iii) the cellulosic material comprises a plurality of pores and (2) a binder

material comprising lime, wherein the lime comprises calcium oxide or calcium hydroxide; and (b) mixing the cellulosic material and the binder material, to generate the composite material.

[0016] In some ~~embodiment~~examples of any one of the subject methods, wherein the cellulosic material is at least partially dried by an external pressure. In some ~~embodiment~~examples, the cellulosic material is at least partially dried in absence of an external source of heat.

[0017] In some ~~embodiment~~examples of any one of the subject methods, the lime comprises calcium oxide and calcium hydroxide.

[0018] In some ~~embodiment~~examples of any one of the subject methods, the binder material further comprises silica. In some ~~embodiment~~examples of any one of the subject methods, a weight ratio of the silica (S) and the lime (L) is between about 1:1 and about 1:5 (S:L). In some ~~embodiment~~examples of any one of the subject methods, a weight ratio of the silica (S) and the lime (L) is about 1:3 (S:L).

[0019] In some ~~embodiment~~examples of any one of the subject methods, a weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 1:10 and about 20:10 (BM:CM). In some ~~embodiment~~examples, the weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 7:10 and about 15:10 (BM:CM). In some ~~embodiment~~examples, the weight ratio of the binder material (BM) to the cellulosic material (CM) is between about 1:10 and about 2:10.

[0020] In some ~~embodiment~~examples of any one of the subject methods, the method further comprises exposing the mixture in (b) to an external stimulus to transform the binding material into a cementitious material. In some ~~embodiment~~examples, the external stimulus comprises one or more members selected from the group consisting of: carbonation, hydration, pressure, and heat. In some ~~embodiment~~examples, the external stimulus comprises hydration. In some ~~embodiment~~examples, the cementitious material comprise silicate.

[0021] In some ~~embodiment~~examples of any one of the subject methods, the cellulosic material comprises one or more members selected from the group consisting of: a bast fiber, leaf, seed, fruit, grass, and wood. In some ~~embodiment~~examples of any one of the subject methods, the cellulosic material comprises a hemp bast fiber.

[0022] In some ~~embodiment~~examples of any one of the subject methods, the composite material is characterized by having a density between about 1 pounds per cubic foot (lb/ft^3) and about 100 lbs/ft^3. In some ~~embodiment~~examples of any one of the subject methods, the composite material is characterized by having a density between about 1 lb/ft^3 and about 30 lbs/ft^3. In some ~~embodiment~~examples of any one of the subject methods, the composite material has a density between about 5 lb/ft^3 and 25 lb/ft^3. In some ~~embodiment~~examples of any one of the subject methods, the composite material is characterized by having a density of at least about 5 lbs/ft^3.

[0023] In some ~~embodiment~~examples of any one of the subject methods, the composite material is usable as a thermal or acoustic insulator for a building.

[0024] In some ~~embodiment~~examples of any one of the subject methods, the composite material exhibits a biocidal activity against a microorganism.

[0025] In some ~~embodiment~~examples of any one of the subject methods, the cellulosic material exhibits enhanced shelf-life as compared to a cellulosic material that does not exhibit the characterization.

[0026] Another ~~aspect~~example of the present disclosure provides a composite building material, wherein the cellulosic material (i) is at least partially delignified, (ii) maintains at least a portion of cellulose crystal structure, and (iii) comprises a plurality of pores, and wherein the cellulosic material is physically or chemically bound to (or within) a binding matrix.

[0027] In some ~~embodiment~~examples, the cellulosic material is a natural fiber, optionally wherein the natural fiber comprises a bast fiber, leaf, seed, fruit, grass, or wood.

[0028] In some ~~embodiment~~examples of any one of the subject composite building materials, a source of the cellulosic material is selected group the group consisting of flax, hemp, kenaf, jute, ramie, isora, nettle, ananas, sisal, abaca, curua, cabuya, palm, opuntia, jipijapa, yucca, cotton, coir, kapok, soya, poplar, calotropis, luffa, bamboo, totora, hardwood, softwood, and a combination thereof.

[0029] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix is an inorganic binding matrix.

[0030] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix comprises a cementitious material comprising cementitious oxides or hydroxides. In some ~~embodiment~~examples, the cementitious material is formed (e.g., cured) by exposure to an external stimulus, optionally wherein the external stimulus comprises carbonation or hydration. In some ~~embodiment~~examples, the cementitious material is formed from akali-activated materials.

[0031] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix comprises lime (calcium oxide or calcium hydroxide) and silica (e.g., amorphous silica).

[0032] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix comprises inorganic polymers or geopolymer cements, optionally wherein the geopolymer cement comprises (i) slag-based, rock-based, or alkali-activated fly ash geopolymer, (ii) slag/fly ash-based geopolymer cement, or (iii) ferro-sialate-based geopolymer cement.

[0033] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix is blended with a volumetric portion of pozzolanic materials, porous ceramic aggregates, or other binding agents that form porous hydrates.

[0034] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix is combined with a concrete admixture comprising foaming agents, blowing agents, or stearate gelling agents.

[0035] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix comprises amorphous silica and/or calcium, aluminum, or magnesium silicates.

[0036] In some ~~embodiment~~examples of any one of the subject composite building materials, the binding matrix exhibits an antibacterial and antifungal activity, optionally wherein the antibacterial and antifungal activity is demonstrated in an alkaline environment ranging between about pH 10 to about pH 14.

[0037] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material has a density between about 1 pounds per cubic foot (lb/ft^3) and about 100 lbs/ft^3. In some ~~embodiment~~examples, the composite building material has a density between about 3 lb/ft^3 and about 50 lbs/ft^3. In some ~~embodiment~~examples, the composite building material has a density between about 5 lb/ft^3 and about 50 lbs/ft^3. In some ~~embodiment~~examples, the composite building material has a density between about 3.7 lb/ft^3 and about 22 lbs/f^{t3}. In some ~~embodiment~~examples, the composite building material has a density between about 10 lb/ft^3 and about 20 lbs/f^{t3}.

[0038] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material has a density of at least about 5 lb/ft^3.

[0039] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material is cured at a temperature between about 30 degrees Freethought (ºF) and about 500 ºF. In some ~~embodiment~~examples, the composite building material is cured at a temperature between about 40 ºF and about 200 ºF. In some ~~embodiment~~examples, the composite building material is cured at a temperature between about 60 ºF and about 100 ºF

[0040] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material is cured at a relative humidity of between about 50 % to about 100 %, to control binding matrix reaction (e.g., hydrate formation) and increase initial and long-term compressive strength. In some ~~embodiment~~examples, the composite building material is cured at a relative humidity of between about 60 % to about 99 %, to control binding matrix reaction (e.g., hydrate formation) and increase initial and long-term compressive strength.

[0041] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material is cured in a controlled environmental (e.g., aforementioned) for between about 1 day to about 50 days. In some ~~embodiment~~examples, the composite building material is cured in a controlled environment for between about 3 days to about 28 days.

[0042] In some ~~embodiment~~examples of any one of the subject composite building materials, wherein a volumetric mix ratio of the cellulosic material (CM) and the binding matrix (BM) is between about 1:1 and about 10:1 (CM:BM).

[0043] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material is mixed in a drum, paddle, or pan mixture (e.g., a drum, paddle, or pan mixer for concrete or mortar). In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material is cast into place, precast molded into place, or continuously extruded into place through ceramic vacuum or vibration extrusion manufacturing equipment.

[0044] In some ~~embodiment~~examples of any one of the subject composite building materials, the composite building material exhibits thermal mass due to favorable hygroscopic pores that experience cyclic water vapor condensation and evaporation reactions.

[0045] Another ~~aspect~~example of the present disclosure provides a method for generating engineered fiber aggregates for composite building material, comprising subjecting a cellulosic material to a pretreatment such that the cellulosic material (i) is at least partially delignified, (ii) maintains at least a portion of cellulose crystal structure, and (iii) comprises a plurality of pores, to generate the engineered fiber aggregates.

[0046] In some ~~embodiment~~examples, the pretreatment comprises selectively depolymerizing the cellulosic material by using liquid pulping or bleaching. In some ~~embodiment~~examples, the bleaching effects increased surface area or surface roughness of the cellulosic material. In some ~~embodiment~~examples, the increased surface area or surface roughness of the cellulosic material is capable of enhancing an increase in chemical or physical coupling (e.g., bonding) between the engineered fiber aggregates and a binder matrix.

[0047] In some ~~embodiment~~examples of any one of the subject methods, the pretreatment (e.g., the selective depolymerization by liquid puling or bleaching) removes, from the cellulosic material, one or more members selected from the group consisting of free lipids, fats, oils, sugars such as hemicellulose, lignin, active molecules, inert molecules, and other contaminants capable of inhibiting chemical or physical bonding between the engineered fiber aggregates and a binding matrix.

[0048] In some ~~embodiment~~examples of any one of the subject methods, the pretreatment (e.g., the selective depolymerization by liquid puling or bleaching) removes, from the cellulosic material, dust particles (i) capable of inhibiting chemical or physical bonding between the engineered fiber aggregates and a binding matrix or (ii) having a size less than or equal to about 1 millimeter.

[0049] In some ~~embodiment~~examples of any one of the subject methods, the pretreatment (e.g., the selective depolymerization by liquid puling or bleaching) enhances shelf-life of the engineered fiber aggregates as compared to without the pretreatment.

[0050] In some ~~embodiment~~examples of any one of the subject methods, the pretreatment (e.g., the selective depolymerization by liquid puling or bleaching) reduces or inhibits (e.g., neutralizes) bacterial or fungal growth on the engineered fiber aggregates as compared to without the pretreatment.

[0051] In some ~~embodiment~~examples of any one of the subject methods, further comprising dewatering the cellulosic material or the engineered fiber aggregates to an ambient water weight (e.g., between about 4 and about 12 % by weight). In some ~~embodiment~~examples, dewatering is performed mechanically to avoid thermal energy input. In some ~~embodiment~~examples, the mechanical dewatering comprises screw-pressing or centrifugal methods. In some ~~embodiment~~examples, the mechanical dewatering avoids shrinkage of a cell wall of the cellulosic material or rupturing of the cell well as compared to a thermal dewatering mechanism.

[0052] In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates exhibit increased porosity as determined by mercury intrusion porosimetry. In some ~~embodiment~~examples, the increased porosity is based at least in part on one or more dewatering mechanisms.

[0053] In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size greater than at least about 1 micrometer. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size greater than at least about 10 micrometers. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size greater than at least about 20 micrometers.

[0054] In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size of at least about 1 micrometer as compared to without the pretreatment. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size of at least about 10 micrometers as compared to without the pretreatment. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment reduces an amount of pores having a size of at least about 20 micrometers as compared to without the pretreatment.

[0055] In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment increases an amount of pores having a size of at most about 20 micrometers as compared to without the pretreatment. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment increases an amount of pores having a size of at most about 10 micrometers as

compared to without the pretreatment. In some ~~embodiment~~examples of any one of the subject methods, wherein the pretreatment increases an amount of pores having a size of at most about 1 micrometer as compared to without the pretreatment.

[0056] In some ~~embodiment~~examples of any one of the subject methods, wherein the engineered fiber aggregates is characterized by exhibiting an increase in pores that reduce convection heat transfer due to the Knudsen effect.

[0057] In some ~~embodiment~~examples of any one of the subject methods, further comprising mixing the engineered fiber aggregates with an additional material comprising one or more members selected from the group consisting of the cementitious binder, geopolymer binder, foaming agents, blowing agents, and stearate gelling agents. In some ~~embodiment~~examples, the additional material is incorporated into at least a portion of the plurality of pores of the engineered fiber aggregates.

[0058] In some ~~embodiment~~examples of any one of the subject methods, further comprising milling the engineered fiber aggregates to an average particle size between about 100 micrometers and about 100 millimeters. In some ~~embodiment~~examples of any one of the subject methods, further comprising milling the engineered fiber aggregates to an average particle size between about 1 micrometers and about 100 millimeters. In some ~~embodiment~~examples of any one of the subject methods, further comprising milling the engineered fiber aggregates to an average particle size between about 1 micrometers and about 51 millimeters.

[0059] In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates exhibit enhanced hygroscopic property as compared to without the pretreatment, wherein the hygroscopic property is characterized by (i) enhanced wicking or uptake of ambient water vapor or (ii) enhanced evaporation thereof upon an exposure to heat.

[0060] In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates exhibit enhanced thermal mass properties (e.g., thermal capacitance or heat capacity) as compared to without the pretreatment. In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates exhibit a thermal mass of between about 500 Joule per kilogram per kelvin (J/kg·K) and about 2500 J/kg·K. In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates exhibit a thermal mass of between about 1000 J/kg·K to about 2100 J/kg·K.

[0061] In some ~~embodiment~~examples of any one of the subject methods, the engineered fiber aggregates have a density (e.g., a dry-bulk density) of less than or equal to about 1000 kilogram per cubic meter (kg/m^3) (or 62 lbs/ft^3). In some ~~embodiment~~examples, the engineered fiber aggregates have a density of less than or equal to about 500 kg/m^3 (or 31 lbs/ft^3). In some ~~embodiment~~examples, the

engineered fiber aggregates have a density of less than or equal to about 300 kg/m^3 (or 19 lbs/ft^3).

[0062] Additional ~~aspect~~example**s** and advantages of the present disclosure will become readily apparent to those skilled in this art from the following detailed description, wherein only illustrative ~~embodiment~~example**s** of the present disclosure are shown and described. As will be realized, the present disclosure is capable of other and different ~~embodiment~~example**s**, and its several details are capable of modifications in various obvious respects, all without departing from the disclosure. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

INCORPORATION BY REFERENCE

[0063] All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference. To the extent publications and patents or patent applications incorporated by reference contradict the disclosure contained in the specification, the specification is int'ended to supersede and/or take precedence over any such contradictory material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0064] The novel features of the invention are set forth with particularity in the appended claims. A better understanding of the features and advantages of the present disclosure will be obtained by reference to the following detailed description that sets forth illustrative embodiments, in which the principles of the invention are utilized, and the accompanying drawings (also "Figure" and "FIG." herein) of which:

[0065] **FIG. 1** shows mercury intrusion porosimetry data of a cellulosic material that is treated with various drying methods.

[0066] **FIG. 2** shows a scanning electron microscopy (SEM) image of a cellulosic material following delignification.

[0067] **FIG. 3** shows an SEM image of another cellulosic material following delignification.

[0068] **FIG. 4** shows an example composite material comprising a cellulosic material and a binder material.

[0069] **FIG. 5** shows an example flowchart of a method for generating a composite material.

DETAILED DESCRIPTION

[0070] While various embodiments of the invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of