(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
23 January 2025 (23.01.2025)

WIPO | PCT

(10) **International Publication Number**
WO 2025/019374 A2

(51) **International Patent Classification:**
C08H 8/00 (2010.01) *C04B 16/02* (2006.01)

(21) **International Application Number:**
PCT/US2024/037925

(22) **International Filing Date:**
12 July 2024 (12.07.2024)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
63/526,952 14 July 2023 (14.07.2023) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: DENSIFIED LIGNOCELLULOSIC FIBERS, CONCRETE REINFORCED WITH SUCH FIBERS, AND METHODS FOR FABRICATION AND USE OF SUCH FIBERS

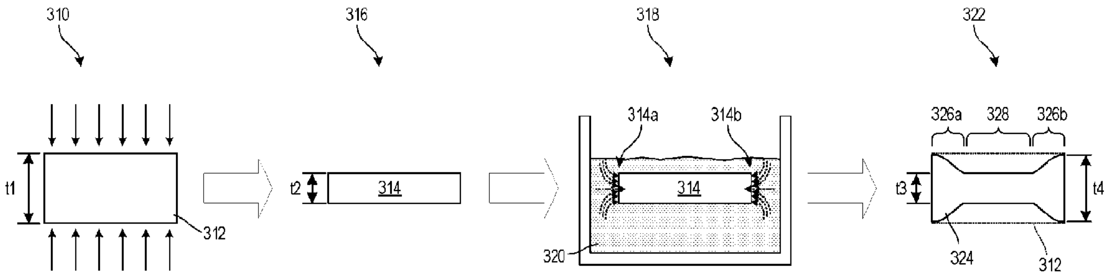

FIG. 3B

(57) **Abstract:** A plant material can be processed such that native lignin therein is degraded, for example, by modifying the native lignin and/or removing at least a portion of the native lignin. A water blocking agent can be formed on and/or within the processed plant material. The processed plant material can be densified and formed into individual lignocellulosic fibers, each having a cross-sectional dimension less than or equal to 5 mm. The lignocellulosic fibers can be mixed into wet concrete or cement and used to reinforce the concrete or cement once dried or set.

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DENSIFIED LIGNOCELLULOSIC FIBERS, CONCRETE REINFORCED WITH SUCH FIBERS, AND METHODS FOR FABRICATION AND USE OF SUCH FIBERS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of and priority to the earlier filing date of U.S. Provisional Application No. 63/526,952, filed July 14, 2023, entitled "High-Density Water-Resistance Lignocellulosic Fibers," which is hereby incorporated by reference herein in its entirety.

FIELD

The present disclosure relates generally to structures formed of plant materials (e.g., wood, bamboo, etc.), and more particularly, to densified lignocellulosic fibers and methods of fabricating and use thereof, for example, to reinforce concrete.

BACKGROUND

Conventional concrete has low tensile strength (2-5 psi) and poor ductility. Concrete is generally heavy (density of about 2,400 kg/m^3) and may be prone to cracking, spalling and blistering. Many of these structural problems can be resolved or alleviated by incorporating fibers into the concrete. This modified material is known as fiber-reinforced concrete and is made by mixing short fibers with cement powder, aggregate (including sand or gravel), and water. Fibers used in the production of fiber-reinforced concrete include those based on steel, glass, carbon, polypropylene and polyethylene.

Carbon fiber typically imparts a superior combination of strength enhancement and chemical resistance but does so at the highest cost. Steel fibers are also associated with high-performance and relatively high cost, but the steel fibers can be difficult to disperse in the concrete and can also be susceptible to corrosion. Glass fibers can provide an attractive balance of physical property improvement at a reasonable cost, but the glass fibers must be based on special grades of alkali-resistant glass. Thermoplastic fibers, such as those based on polypropylene or polyethylene can be easy to disperse and have the lowest cost. These polyolefin fibers are flexible and can provide good impact and crack-resistance, but generally do not significantly improve the tensile strength of the concrete. Carbon fibers, glass fibers, and polyolefin fibers all have smooth, non-porous, low-energy surfaces that tend to bond poorly to aqueous slurries of cements, such as Portland cement. In most cases, these fibers have simple rectangular or cylindrical shapes.

There are additional environmental concerns. The production of concrete creates significant CO_2 emissions (about 0.93 kg CO_2 per kg of concrete). To date, about 4-8% of the emitted carbon dioxide on the planet is believed to come from concrete. Furthermore, conventional fibers used to reinforce concrete, including glass fibers, steel fibers, and carbon fibers, all have large emission footprints.

Aspects of the present disclosure may address one or more of the above-noted problems and disadvantages, among other things.

SUMMARY

Aspects of the present disclosure provide lignocellulosic fibers, and methods for fabricating such lignocellulosic fibers from initial plant material (or other fibrous biomass). In some aspects, the disclosed fibers can be permeated with one or more chemical substances that reduces their propensity for absorbing water, which may improve their geometric stability in aqueous environments. In some aspects, this feature can render the lignocellulosic fibers suitable for use in reinforcing concrete. Alternatively or additionally, in some aspects, the treatment with chemical substances can regulate a swelling rate due to water absorption of the lignocellulosic fibers (e.g., prior to mixing with wet concrete, during mixing with wet concrete, and/or during drying of the concrete), such that axial ends of the lignocellulosic fibers preferentially swell, for example, to form a dog-bone shape. In some aspects, the dog-bone shape help locks the lignocellulosic fibers in place once the concrete is dried or set. Alternatively or additionally, in some aspects, the lignocellulosic fibers can be mechanically processed to have a non-rectangular shape in side view, which shape may also help lock the fibers in place within dried concrete. In some aspects, surfaces of the lignocellulosic fibers can be further modified to enhance engagement with the surrounding concrete, e.g., by increasing surface energy of the fibers, modifying surface topography of the fibers, and/or by increasing the potential for bonding of the fibers to the concrete.

In one or more aspects, a method can comprise processing an initial plant material such that native lignin therein is degraded. The processing can comprise modifying the native lignin within the initial plant material and/or removing at least a portion of the native lignin from the initial plant material. The method can further comprise forming a water blocking agent on and/or within the processed plant material. The method can also comprise densifying the processed plant material. The method can further comprise forming the processed plant material into individual lignocellulosic fibers. Each lignocellulosic fiber can have a cross-sectional dimension less than or equal to 5 mm.

In one or more aspects, a structure can comprise a plurality of lignocellulosic fibers and a water blocking agent. Each fiber can have a cross-sectional dimension less than or equal to 5 mm. The water blocking agent can be on and/or within the plurality of lignocellulosic fibers. In some aspects, the structure can further comprise concrete, and the plurality of lignocellulosic fibers can be dispersed within the concrete.

Any of the various innovations of this disclosure can be used in combination or separately. This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the detailed description. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. The foregoing and other objects, features, and advantages of the disclosed technology will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the present disclosure will hereinafter be described with reference to the accompanying drawings, which have not necessarily been drawn to scale. Where applicable, some elements may be simplified or otherwise not illustrated in order to assist in the illustration and description of underlying features. Throughout the figures, like reference numerals denote like elements.

FIG. 1A is a simplified process flow diagram illustrating a method for fabricating and using lignocellulosic fibers, according to one or more aspects of the disclosed subject matter.

FIG. 1B is a simplified process flow diagram illustrating a method of modifying a shape of lignocellulosic fibers, according to one or more embodiments of the disclosed subject matter.

FIG. 2 illustrates radial, longitudinal, and rotary cut pieces of natural wood, as well as a cross-section in the radial-tangential plane of natural wood, any of which pieces may be subjected to lignin degradation, water blocking agent treatment, densification, and fiber formation, according to one or more aspects of the disclosed subject matter.

FIG. 3A illustrates an exemplary lignocellulosic fiber having a non-complex shape, according to one or more aspects of the disclosed subject matter.

FIG. 3B illustrates aspects of forming a lignocellulosic fiber with a complex shape, according to one or more aspects of the disclosed subject matter.

FIG. 4 is a graph of experimentally measured swelling of the thickness of densified, lignin-modified wood (MettleWood) fibers versus exposure time to an aqueous environment for different loading of water blocking agent loading.

FIGS. 5A-5D are photographs of fractured fiber-reinforced concrete blocks, showing the shape of densified, lignin-modified wood fibers therein after concrete drying; FIG. 5A is a top plan view of the fractured fiber-reinforced concrete blocks; FIG. 5B is an enlarged view of FIG. 5A showing the shape of the densified, lignin-modified wood fibers; FIG. 5C is a cross-sectional view of the fractured fiber-reinforced concrete blocks; and FIG. 5D is an enlarged view of FIG. 5C showing the shape of densified, lignin-modified wood fibers therein after concrete drying.

FIGS. 6A-6B is a photograph of densified, lignin-modified wood fibers before (dry) and after (wet) exposure to an aqueous environment, illustrating the differential swelling of the ends of the fibers; FIG. 6A is a top plan view of the densified, lignin-modified wood fibers before (dry) and after (wet) exposure to an aqueous environment; and FIG. 6B is an enlarged view of FIG. 6A showing an axial end of the dry lignin-modified wood fibers and wet lignin-modified wood fibers.

DETAILED DESCRIPTION

General Considerations

For purposes of this description, certain aspects, advantages, and novel features of the disclosed subject matter are described herein. The disclosed methods and systems should not be construed as being limiting in any way. Instead, the present disclosure is directed toward all novel and nonobvious features and aspects disclosed herein, alone and in various combinations and sub-combinations with one another. The methods and systems are not limited to any specific aspect or feature or combination thereof, nor do the disclosed aspects require that any one or more specific advantages be present, or problems be solved. The technologies from any aspect or example can be combined with the technologies described in any one or more of the other aspects or examples. In view of the many possible aspects to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated aspects of the disclosure are exemplary only and should not be taken as limiting the scope of the disclosed technology.

Although the operations of some of the disclosed methods are described in a particular, sequential order for convenient presentation, it should be understood that this manner of description encompasses rearrangement, unless a particular ordering is required by specific language set forth below. For example, operations described sequentially may in some cases be rearranged or performed concurrently. Moreover, for the sake of simplicity, the attached figures may not show the various ways in which the disclosed methods can be used in conjunction with other methods. Additionally, the description sometimes uses terms like “provide” or “achieve” to describe the disclosed methods. These terms are high-level abstractions of the actual operations that are performed. The actual operations that correspond to these terms may vary depending on the particular implementation and are readily discernible by one skilled in the art.

The disclosure of numerical ranges should be understood as referring to each discrete point within the range, inclusive of endpoints, unless otherwise noted. Unless otherwise indicated, all numbers expressing quantities of components, molecular weights, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term “about.” Accordingly, unless otherwise implicitly or explicitly indicated, or unless the context is properly understood by a person skilled in the art to have a more definitive construction, the numerical parameters set forth are approximations that may depend on the desired properties sought and/or limits of detection under standard test conditions/methods, as known to those skilled in the art. When directly and explicitly distinguishing aspects from discussed prior art, the numbers are not approximates unless the word “about,” “substantially,” or “approximately” is recited. Whenever “substantially,” “approximately,” “about,” or similar language is explicitly used in combination with a specific value, variations up to and including 10% of that value are intended, unless explicitly stated otherwise.

Directions and other relative references may be used to facilitate discussion of the drawings and principles herein but are not intended to be limiting. For example, certain terms may be used such as “inner,” “outer,” “upper,” “lower,” “top,” “bottom,” “interior,” “exterior,” “left,” right,” “front,” “back,” “rear,” and the like. Such terms are used, where applicable, to provide some clarity of description when dealing with relative relationships, particularly with respect to the illustrated aspects. Such terms are not, however, intended to imply absolute relationships, positions, and/or orientations. For example, with respect to an object, an “upper” part can become a “lower” part simply by turning the object over. Nevertheless, it is still the same part, and the object remains the same.

As used herein, “comprising” means “including,” and the singular forms “a” or “an” or “the” include plural references unless the context clearly dictates otherwise. The term “or” refers to a single element of stated alternative elements or a combination of two or more elements unless the context clearly indicates otherwise.

Although there are alternatives for various components, parameters, operating conditions, etc. set forth herein, that does not mean that those alternatives are necessarily equivalent and/or perform equally well. Nor does it mean that the alternatives are listed in a preferred order, unless stated otherwise. Unless stated otherwise, any of the groups defined below can be substituted or unsubstituted.

Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one skilled in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below.

The materials, methods, and examples are illustrative only and not intended to be limiting. Features of the presently disclosed subject matter will be apparent from the following detailed description and the appended claims.

Overview of Terms

The following are provided to facilitate the description of various aspects of the disclosed subject matter and to guide those skilled in the art in the practice of the disclosed subject matter.

Plant Material: A portion (e.g., a cut portion, via mechanical means or otherwise) of any photosynthetic eukaryote of the kingdom *Plantae* in its native state as grown. In some aspects, the plant material comprises wood (e.g., hardwood or softwood) or bamboo (e.g., any of *Bambusoideae*, such as but not limited to *Moso*, *Phyllostachys vivax*, *Phyllostachys viridis*, *Phyllostachys bambusoides*, *Phyllostachys nigra*, *Guadua angustifolia*, *Bambusa emeiensis*, *Arundinaria gigantea*, *Chusquea culeou*, and *Bambusa vulgaris Vittata*). For example, the natural wood can be any type of hardwood (e.g., having a native lignin content in a range of 18-25 wt%) or softwood (e.g., having a native lignin content in a range of 25-35 wt%), such as, but not limited to, basswood, poplar, ash, alder, aspen, balsa wood, beech, birch, cherry, butternut, chestnut, cocobolo, elm, hickory, maple, oak, padauk, plum, walnut, willow, yellow poplar, bald cypress, cedar, cypress, douglas fir, fir, hemlock, larch, pine, redwood, spruce, tamarack, juniper, and yew. In other aspects, the plant material comprises reed (e.g., any of common reed (*Phragmites australis*), giant reed (*Arundo donax*), Burma reed (*Neyraudia reynaudiana*), reed canary-grass (*Phalaris arundinacea*), reed sweet-grass (*Glyceria maxima*), small-reed (*Calamagrostis species*), paper reed (*Cyperus papyrus*), bur-reed (*Sparganium species*), reed-mace (*Typha species*), cape thatching reed (*Elegia tectorum*), and thatching reed (*Thamnochortus insignis*)), hemp (*Cannabis sativa*), jute, ramie, flax, sisal, or other grass (e.g., a species selected from the *Poales* order or the *Poaceae* family). Alternatively, in some aspects, the plant material can be any type of fibrous plant composed of lignin and cellulose. For example, the plant material can be bagasse (e.g., formed from processed remains of sugarcane or sorghum stalks), straw (e.g., formed from processed remains of cereal plants, such as rice, wheat, millet, or maize), kenaf, or coir from coconut husks.

Lignin-degraded plant material: Plant material that has been modified by one or more chemical treatments to (a) modify the native lignin therein and/or (b) partially remove the native lignin therein (i.e., partial delignification). In some aspects, the lignin-degraded plant material can substantially retain the native microstructure formed by cellulose-based cell walls of the natural plant material.

Partial Delignification: The removal of some (e.g., at least 5%) but not all (e.g., less than or equal 95%) of native lignin (e.g., on a weight percent basis) from the plant material. In some aspects, the partial delignification can be performed by subjecting the plant material to one or more chemical treatments. In some aspects, the lignin content after partial delignification can be in a range of 0.9-23.8 wt% for hardwood or bamboo, or in a range of 1.25-33.25 wt% for softwood. Lignin content within the plant material before and after the partial delignification can be assessed using known techniques in the art, for example, Laboratory Analytical Procedure (LAP) TP-510-42618 for "Determination of Structural Carbohydrates and Lignin in Biomass," Version 08-03-2012, published by National Renewable Energy Laboratory (NREL), and ASTM E1758-01(2020) for "Standard Test Method for Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography," published by ASTM International, both of which are incorporated herein by reference. In some aspects, the partial delignification process can be, for example, as described in U.S. Publication No. 2020/0223091, published July 16, 2020 and entitled "Strong and Tough Structural Wood Materials, and Methods for Fabricating and Use Thereof," and U.S. Publication No. 2022/0412002, published December 29, 2022 and entitled "Bamboo Structures, and Methods for Fabrication and Use Thereof," which delignification and densification processes are incorporated herein by reference.

Lignin modification: *In situ* altering of one or more properties of native lignin in the plant material, while retaining at least some (e.g., most) of the altered lignin within the plant material. In some aspects, the lignin content of the plant material prior to and after the *in situ* modification can be substantially the same, for example, such that the *in situ* modified plant material retains at least 90% (e.g., removing no more than 10%, or no more than 1%, of the native lignin content) of the native lignin content. In some aspects, the plant material can be *in situ* modified (e.g., by chemical reaction with OH^-) to depolymerize lignin, with the depolymerized lignin being retained within the plant material microstructure. In some aspects, the modified lignin has shorter macromolecular chains than that of native lignin in the pieces of natural plant material, and/or the modified lignin has more exposed functional groups on its surface as compared to native lignin of corresponding natural plant material. Alternatively or additionally, the lignin modification can reduce the molecular weight of the lignin (as compared to native lignin) but not to the point that the lignin becomes soluble in water (e.g., at the temperatures involved in the lignin modification, such as 20-200 °C). The lignin content within the plant material before and after lignin modification can be assessed using known techniques in the art, for example, Laboratory Analytical Procedure (LAP) TP-510-42618 for "Determination of Structural Carbohydrates and Lignin in Biomass," Version

08-03-2012, published by National Renewable Energy Laboratory (NREL), ASTM E1758-01(2020) for "Standard Test Method for Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography," published by ASTM International, and/or Technical Association of Pulp and Paper Industry (TAPPI), Standard T 222-om-83, "Standard Test Method for Acid-Insoluble Lignin in Wood," all of which are incorporated herein by reference. In some aspects, the lignin modification process can be, for example, as described in U.S. Publication No. 2024/0083067, published March 14, 2024, and entitled "Waste-free Processing for Lignin Modification of Fibrous Plant Materials, and Lignin-modified Fibrous Plant Materials," which lignin modification processes are incorporated herein by reference.

Densified or Compressed Plant Material: A plant material that has been compressed to have a reduced thickness. In some aspects, the thickness has been reduced by a factor of at least two. In some aspects, the densified plant material can have a density greater than that of the starting plant material, for example, a density of at least 1 g/cm^3, such as at least 1.1 g/cm^3 or even at least 1.2 g/cm^3 (e.g., 1.3-1.5 g/cm^3). For example, the densified plant material can be formed as described in, but not limited to, U.S. Patent No. 11,130,256, issued September 28, 2021, entitled "Strong and Tough Structural Wood Materials, and Methods for Fabricating and Use Thereof," and U.S. Publication No. 2022/0412002, published December 29, 2022 and entitled "Bamboo Structures, and Methods for Fabrication and Use Thereof," each of which is incorporated herein by reference. In some aspects, the densified plant material can be cut, machined, molded, or otherwise mechanically altered to form one or more lignocellulosic fibers.

Axial direction: A direction (e.g., L in FIG. 2) along which a plant grows from its roots or from a trunk thereof, with cellulose fibers forming cell walls of the plant being generally aligned with the fiber direction. In some cases, the axial direction may be generally vertical or correspond to a direction of its water transpiration stream. This is in contrast to the radial direction (e.g., R in FIG. 2), which extends from a center portion of the plant outward.

Crosslinking: A chemical process by which a small reactive molecule (e.g., ≤500 g/mole) reacts with a polymer or macromolecule (e.g., amorphous cellulose and/or hemicellulose of cell walls in the plant material, and/or lignin in the plant material) in a manner that reduces freedom of motion of the polymer or macromolecule on a molecular level. In some aspects, crosslinking of amorphous cellulose or hemicellulose (e.g., via a stabilizing agent) can prevent, or at least reduce a rate of, volumetric expansion as it absorbs water. Alternatively or additionally, in some aspects, crosslinking can cause lignin molecules (e.g., degraded) to become water insoluble.

Reaction Product: The product of a reaction between at least two reactants. In some aspects, the reaction product is the product of a chemical reaction between one or more nucleophiles (e.g., Lewis base) and one or more electrophiles (e.g., Lewis acid). In some aspects, the reaction product can be a product of a reaction where all atoms present in the reactants are maintained in the product. In other aspects, the reaction product can be a product of a reaction where not all atoms present in the reactants are maintained in the product. In some aspects, the reaction product has a molecular weight less than or equal to 500 g/mole. In some aspects, the reaction product is highly soluble in water. In some aspects, the reaction product is an adduct.

Thickness: A cross-sectional dimension of a piece of plant material that is aligned with the direction of compression (e.g., 304 in FIG. 3A) for this disclosure. In some aspects, the thickness dimension may be less than 25.4 mm (1.0 inches), for example, less than or equal to 6.4 mm (0.25 inches), such as greater than zero inches to a value of 6.4 mm (0.25 inches). In some aspects, the thickness dimension is aligned with the radial direction (e.g., R in FIG. 2) of the plant material. In other aspects, the thickness dimension is aligned with the tangential direction (e.g., T in FIG. 2) of the plant material. In still other aspects, the thickness dimension is aligned with a mixture of the tangential and radial directions of the plant material. Alternatively, in some aspects, the direction of the thickness dimension is at a non-orthogonal angle with respect to one or both of the axial and radial directions. In some aspects, the thickness direction corresponds to a minimum cross-sectional dimension of the piece of plant material.

Water Blocking Agent Precursors: Chemical species that can be reacted to form a water blocking agent. In some aspects, the water blocking agent precursors comprise an electrophile and a nucleophile. In certain aspects, the water blocking agent precursors are small molecules (e.g., having a molecular weight less than 500 g/mole, such as a molecular weight ranging from greater than 0 g/mole to a molecular weight of 500 g/mole).

Water Blocking Agent: An agent provided to a lignocellulosic fiber to inhibit swelling thereof due to water infiltration. In some aspects, the water blocking agent can reduce the level of swelling of the lignocellulosic fiber in a saturated state relative to the level of swelling that would be experienced when a non-treated lignocellulosic fiber is in a saturated state. In some aspects, the water blocking agent can reduce the rate of swelling of the lignocellulosic fiber relative to the rate of swelling that would be experienced in a non-treated lignocellulosic fiber. In some aspects, the water blocking agent is a product of a reaction between nucleophile and electrophile. In some aspects, the water blocking agent is formed in the reaction of nucleophile and electrophile and has the potential to crosslink certain polysaccharides (e.g., amorphous cellulose and/or hemicellulose) at specific regions within the plant cell wall. In some aspects, the water blocking agent can be formed prior to infiltration into the lignocellulosic material. In some aspects, the water blocking agent is a small molecule (e.g., less than 500 g/mole) that is hydrophilic. In certain aspects, the water blocking agent can be highly water soluble. In some aspects, the water blocking agent has the potential to crosslink lignin (e.g., degraded) within the plant material. In some aspects, precursors to the water blocking agent, specifically nucleophile molecules and electrophile molecules, can be infiltrated into the lignocellulosic material in a first step. These molecules will generally be smaller and more mobile than the water blocking agent. Thus, the water blocking agent precursors could be delivered to the target sites (amorphous cellulose and hemicellulose) and a faster rate than that of the water blocking agent. Subsequent to delivery at the target site, the precursors can react to form the water blocking agent. The water blocking agent that has been formed within the lignocellulosic material can subsequently crosslink amorphous cellulose, hemicellulose and/or degraded lignin at a later stage of the process. In some aspects, the formulation for and/or the forming of the water blocking agent can be similar to that for the stabilizing agents described in International Application No. PCT/US24/25554, filed April 19, 2024 and entitled “Plant Materials with Improved Water Stability, and Methods for Fabrication Thereof," which description is incorporated herein by reference.

Introduction

Disclosed herein are lignocellulosic fibers derived from plant material (e.g., wood or other biomass fibers), methods for forming such lignocellulosic fibers, and uses of such lignocellulosic fibers, for example, in reinforcing concrete. In some aspects, the plant material can be subject to one or more treatments that degrades native lignin therein (e.g., by modifying the lignin and/or removing some, but not all, lignin), subjected to densification (e.g., via one or multiple compression processes), and mechanically processed into individual fibers. In some aspects, prior to and/or during densification, a water blocking agent can be provided on and/or within the treated plant material, which can reduce swelling (or at least control a swelling rate) of the resulting fibers when exposed to water to improve dimensional stability thereof.

In some aspects, the fibers with water blocking agent may still exhibit swelling when exposed to water; however, the swelling rate (e.g., via loading of the water blocking agent) and/or duration of the water exposure can be controlled to provide the fiber with a complex, non-rectangular shape (in side view), which shape may enhance the reinforcing capabilities of the fibers when embedded within dried concrete. For example, axial ends of the lignocellulosic fibers may be preferentially swelled (e.g., in a plane perpendicular to an axial direction of the fiber), while the interior (e.g., intermediate or middle portion) of the lignocellulosic fibers experiences relatively little or no swelling, thereby forming a dog-bone shape. In some aspects, the swelling may be achieved by immersing the lignocellulosic fibers in aqueous solution (e.g., containing the water blocking agent or precursors thereof) prior to combining with concrete components. Alternatively or additionally, the axial ends of the lignocellulosic fibers can preferentially swell *in situ*, for example, due to water exposure during the mixing and/or drying (or setting) phases of the concrete, so as to lock the lignocellulosic fibers in place while the dried concrete sets.

In some aspects, the fibers can be further modified to enhance their capability for reinforcing concrete. For example, the fibers can be mechanically processed to adopt a complex (e.g., non-rectangular) shape without relying on water-induced swelling. Alternatively or additionally, in some aspects, the surfaces of the lignocellulosic fibers can be processed to improve engagement with the surrounding concrete. For example, the surfaces of the lignocellulosic fibers can be treated with a pulping agent, an oxidizing agent, an acidic agent, or a coating. Alternatively or additionally, the topography of the surfaces of the lignocellulosic fibers can be altered, for example, via embossing, etching, and/or stamping. Alternatively or additionally, the surface of the lignocellulosic fibers can be altered via heat treatment.

In some aspects, the lignocellulosic fibers can be dispersed in aqueous slurries of concrete and/or cement in the production of fiber reinforced concrete or cement. For example, these reinforcing fibers can have modulus values of about 25 GPa to about 50 GPa, which is mostly retained (e.g., 80% or more) when the fibers are dispersed in an aqueous concrete or cement slurry. In contrast, wood that is simply compressed, cut into reinforcing fibers, and then dispersed in an aqueous concrete or cement slurry rapidly swells and loses all or most of the increased modulus properties that might have been obtained in the compression process. The excellent dimensional stability of the reinforcing fibers of the present disclosure also helps to ensure that tight mechanical interlocking is achieved between the concrete and the dispersed reinforcing fibers at the interface of these two materials in the reinforced concrete. This effect is further enhanced in examples involving reinforcing fibers with complex shapes and/or surface modification.

In some aspects, the disclosed reinforcing fibers exhibit good adhesion to the cement in the slurry. Moreover, the thermal expansion coefficient of the fibers can be about 1×10^{-5} m/(m·°C), which allows the dispersed reinforcing fibers to expand and contract in concert with that of the concrete or cement matrix. The sustained, intimate connection between the dispersed reinforcing fibers and the concrete/cement allows the reinforcing fibers to structurally support the concrete or cement matrix, especially under bending or tensile stresses. Thus, concrete or cement that is reinforced with the reinforcing fibers of the present disclosure exhibits improved tensile strength, improved bending strength, and improved resistance to cracking.

In some aspects, the disclosed reinforcing fibers also have a favorable carbon footprint. For example, the disclosed reinforcing fibers can be incorporated into specialty concrete that is associated with an exceptionally low carbon dioxide emission rate. For example, Kajima Corporation has recently developed a specialty concrete, known as SUICOM, which is formulated with granulated blast furnace slag. This type of concrete is capable of absorbing substantial levels of carbon dioxide. In some cases, the SUICOM concrete can reduce CO_2 emissions by as much as 60% compared to that of conventional concrete. Composites based on the disclosed reinforcing fibers with such a specialty concrete have a substantially improved carbon footprint compared to that of conventional concrete.

Fabrication Method Examples

FIG. 1A illustrates aspects of a method 100 for fabricating lignocellulosic fibers, or a structure comprising lignocellulosic fibers. The method 100 can initiate at process block 102, where one or more plant material pieces can be provided. In some aspects, the provision of process block 102 can include cutting, removing, or otherwise separating the piece from a parent plant. In some aspects, the parent plant can be small diameter or young plant material (e.g., tree, bamboo stalk, etc.). In some aspects, the cutting can form the plant material into veneers, strips, pieces, or strands, for example, having a thickness less than or equal to 25.4 mm (e.g., ≤ 6.4 mm). Optionally, in some aspects, the preparing can include pre-processing of the piece of natural plant material, for example, cleaning to remove any undesirable material or contamination in preparation for subsequent processing, forming the natural plant material into a particular shape in preparation for subsequent processing (e.g., slicing into smaller strips), or any combination of the foregoing. In some aspects, the plant material has a native lignin content less than or equal to 15 wt%.

In some aspects, the plant material is natural wood, which has a unique three-dimensional porous microstructure comprising and/or defined by various interconnected cells. For example, FIG. 2 illustrates a hardwood microstructure 210 where vessels 212 are disposed within a hexagonal array of wood fiber cells 216 in a longitudinally-extending cell region. The vessels and fibers cells can extend along longitudinal direction, L, of the wood. Thus, the lumen of each vessel 212 can have an extension axis 214 that is substantially parallel to the longitudinal direction, L, and the lumen of each fiber cell 216 can have an extension axis 218 that is substantially parallel to the longitudinal direction, L. Arranged between adjacent regions along tangential direction, T, is a radially-extending cell region, where a plurality of ray cells 220 are disposed. The ray cells 220 can extend along radial direction, R, of the wood. Thus, the lumen of each ray cell 220 can have an extension axis 222 that is substantially parallel to the radial direction, R, of the wood. An intracellular lamella is disposed between the vessels 212, fiber cells 216, and ray cells 220, and serves to interconnect the cells together. Softwoods can have a similar microstructure structure as that of hardwood, but with the vessels and wood fibers being replaced by tracheids that extend in the longitudinal direction, L, of the wood.

The cut direction of the original piece of wood can dictate the orientation of the cell lumina in the final structure. For example, in some aspects, a piece of natural wood can be cut from a trunk 202 of tree 200 in a vertical or longitudinal direction (e.g., parallel to longitudinal wood growth direction, L) such that lumina of longitudinally-extending cells are oriented substantially parallel to a major face (e.g., largest surface area) of the longitudinal-cut wood piece 206. In the longitudinal-cut wood piece 206, the tangential direction, T, can be substantially perpendicular to the major face. Alternatively, in some aspects, the piece of natural wood can be cut in a horizontal or radial direction (e.g., perpendicular to longitudinal wood growth direction, L) such that lumina of longitudinally-extending cells are oriented substantially perpendicular to the major face of the radial-cut wood piece 204. Alternatively, in some aspects, the piece of natural wood can be cut in a rotation direction (e.g., perpendicular to the longitudinal wood growth direction L and along a circumferential direction of the trunk 202) such that lumina of longitudinal cells are oriented substantially parallel to the major face of the rotary-cut wood piece 208. In some aspects, the piece of natural wood can be cut at any other orientation between longitudinal, radial, and rotary cuts. In some aspects, the cut orientation of the wood piece may influence mechanical properties of the final structure.

Returning to FIG. 1A, the method 100 can proceed to decision block 104, where it is determined if lignin within the plant material should be degraded, for example, via partial delignification (for example, using the delignification processes disclosed in either U.S. Publication No. 2020/0223091 or U.S. Publication No. 2022/0412002, incorporated by reference above) and/or lignin modification (for example, using the lignin modification process described in U.S. Publication No. 2024/0083067, incorporated by reference above).

If degradation via modification is desired, the method 100 can proceed to process block 106, where the plant material can be infiltrated with a loading solution. Loading solutions can include aqueous solutions of sodium hydroxide (e.g., concentrations between 0-15.0%, inclusive). Alternatively or additionally, loading solutions can comprise sodium sulfite and/or oxidizing agents, such as ozone, oxygen, hydrogen peroxide, and organic peroxides. In some aspects, loading solutions can be water-based. In certain aspects, the loading solution can comprise one or more non-volatile amines. In particular aspects, the non-volatile amine can be ethanolamine, diethanolamine, triethanolamine, hydroxylamine, triethylamine, hexylamine, butylamine, dibutylamine, methanolamine, dimethanolamine, trimethanolamine, propanolamine, dipropanolamine, tripropanolamine, 2-amino-2-methyl-1-propanol, or valinol. In some aspects, the plant material can be submerged in the loading solution. For example, the submerged plant material can be subjected to one or more vacuum cycles in order to help facilitate absorption of the loading solution into the plant material. Alternatively, positive pressure can be applied to the system to facilitate faster absorption rates. Absorption of the loading solution can occur at a temperature between about 20-100° C, inclusive. Absorption of the loading solution can be conducted for a period of time that is sufficient to achieve a uniform distribution of loading solution within the plant material. During this process, the moisture content of the plant material can be increased from a first moisture content of about 1-20%, inclusive, to a second moisture content of about 15-100%, inclusive. As used herein, the term ‘moisture content’ is defined as 100 percent multiplied by the water mass in a sample divided by the dry wood mass.

Alternatively or additionally, in some aspects, the loading solution can contain at least one chemical component that has OH^- ions or is otherwise capable of producing OH^- ions in solution. In some aspects, one, some, or all of the chemicals in the loading solution can be alkaline. In some aspects, the loading solution includes NaOH, LiOH, KOH, Na_2O, or any combination thereof. Exemplary combinations of chemicals can include, but are not limited to, NaOH, NaOH + Na_2SO_3/Na_2SO_4, NaOH + Na_2S, NaOH + Na_2SO_3, NaOH/ NaH_2O_3 + AQ, NaOH/Na_2S + AQ, NaOH + Na_2SO_3 + AQ, Na_2SO_3 + NaOH + CH_3OH + AQ, NaOH + Na_2Sx, where AQ is Anthraquinone, any of the foregoing with NaOH replaced by LiOH or KOH, or any combination of the foregoing. In some aspects, the concentration of the chemicals for lignin modification can be at a concentration of 5 wt% or less, for example, in a range of 1-4 wt%, inclusive. In some aspects, the immersion of the plant material in loading solution can be performed without heating, e.g., at room temperature (20-30 °C, such as ~22-23 °C). In some aspects, the loading solution is not agitated in order to avoid disruption to the native cellulose-based microstructure of the plant material piece(s).

For example, in some aspects, plant material pieces(s) can be immersed in a chemical solution (e.g., 2-5% NaOH) in a container. The container can then be placed in a vacuum box and subjected to vacuum (e.g., 0.1 MPa). In this way, the air inside of the plant material can be drawn out and absorption of the solution into the plant material piece occurs at a faster rate. The process can be repeated more than once (e.g., 3 times), such that the channels inside the plant material piece can be filled with the chemical solution (e.g., about 2 hours). After this process, the moisture content can increase (e.g., from ~10% for natural wood to ~70% or greater).

The method 100 can proceed to process block 108, where the infiltrated plant material piece can be subjected to heat and/or pressure. For example, after absorbing the loading solution, the treated plant material can be subjected to heat and pressure to promote reactions between the absorbed loading solution and the lignin in the plant material. The temperature associated with this process can be in a range of 20-200° C, inclusive. The gauge pressure can be 100-1,200 MPa, inclusive. In some aspects, higher pressure can prevent, or at least reduce the amount of, water in the plant material from evaporating when the temperature is greater than about 100° C.

For example, treated wood can be subjected to a pressure of about 700-850 MPa and a temperature of about 150-200° C for a period of about 1-5 hours. Under these conditions, lignin in the wood can be partially degraded or otherwise modified in a manner that promotes softening of the wood, especially at elevated temperature. Partial degradation generally involves reducing the molecular weight of the lignin, but not to the point that the lignin becomes water soluble. In some aspects, the temperature of the wood that has been infiltrated with loading solution can be adjusted to either increase or decrease the degree of degradation of the lignin in the wood. After degradation, the wood can then be cooled to about 20° C and the gauge pressure on the wood can be reduced to about 0 MPa.

In some aspects, the heating can be achieved via steam heating, for example, via steam generated in an enclosed reactor (e.g., pressure reactor), via a steam flow in a flow-through reactor, and/or via steam from a superheated steam generator. Alternatively or additionally, in some aspects, the heating of process block 108 can be achieved via dry heating, for example, via conduction and/or radiation of heat energy from one or more heating elements without separate use of steam.

In some aspects, the infiltrated plant material piece(s) can be subjected to the elevated temperature for a first time period of, for example, 1-10 hours (e.g., depending on the size of the plant material piece, with thicker pieces requiring longer heating times). In some aspects, after the first time period, any steam generated by heating of the infiltrated plant material piece(s) can be released, for example, by opening a pressure release (e.g., relief valve) of the reactor. For example, in some aspects, the pressure release can be effective to remove ~50% of moisture in the modified plant material piece(s). For example, in some aspects, the now softened plant material piece(s) can have a moisture content in a range of 30-50 wt%, inclusive.

In some aspects, the infiltration and heating of the plant material piece can be effective to modify the lignin therein, for example, hydroxide ions can hydrolyze ether linkages, which shortens the lignin macromolecular chains and softens the plant material piece. In addition, hydroxide ions can hydrolyze hemicellulose. This process can produce acidic degradation products that can react with the alkaline solution (e.g., NaOH) and form neutral salts. In some aspects, no black liquor is observed during the lignin modification process, and the degradation products from hemicellulose and lignin can be completely immobilized within the channels of the softened plant material piece. In some aspects, since all chemicals are consumed in the process, the softened plant material piece can exhibit a neutral pH.

The method 100 can proceed to decision block 110, where it is determined if rinsing is desired. If rinsing is desired, the method 100 can proceed to process block 114, where the treated plant material can be rinsed, for example, with a solvent, such as but not limited to, de-ionized (DI) water, alcohol (e.g., ethanol, methanol, isopropanol, etc.), or any combination thereof. In some aspects, the treated plant material can thereafter be soaked in or rinsed with water to remove a portion of the lignin that has been degraded to the point of becoming soluble in water.

If partial delignification is instead desired at decision block 104, the method 100 can proceed to process block 112, where the plant material can be subjected to one or more chemical treatments to remove at least some lignin therefrom, for example, by immersion of the plant material piece (or portion(s) thereof) in a chemical solution associated with the treatment. In some aspects, each chemical treatment or only some chemical treatments can be performed under vacuum, such that the solution(s) associated with the treatment is encouraged to fully penetrate the cell walls and lumina of the plant material. Alternatively, in some aspects, the chemical treatment(s) can be performed under ambient pressure conditions or elevated pressure conditions (e.g., ~ 6-8 bar). In some aspects, each chemical treatment or some chemical treatments can be performed at any temperature between ambient (e.g., ~ 23 °C) and an elevated temperature where the solution associated with the chemical treatment is boiling (e.g., ~ 100-160 °C). In some aspects, the solution is not agitated in order to minimize the amount of disruption to the native cellulose-based microstructure of the plant material piece(s).

In some aspects, the immersion time can be in a range of 0.1 to 96 hours, inclusive, for example, 1-12 hours, inclusive. The amount of time of immersion within the solution may be a function of the amount of lignin to be removed, type of plant material, size of the plant material piece, temperature of the solution, pressure of the treatment, and/or agitation. For example, smaller amounts of lignin removal, smaller plant material piece size (e.g., cross-sectional thickness), higher solution temperature, higher treatment pressure, and agitation may be associated with shorter immersion times, while larger amounts of lignin removal, larger plant material piece size, lower solution temperature, lower treatment pressure, and no agitation may be associated with longer immersion times.

In some aspects, the loading solution can include sodium hydroxide (NaOH), lithium hydroxide (LiOH), potassium hydroxide (KOH), sodium sulfite (Na_2SO_3), sodium sulfide (Na_2S), Na_nS (where n is an integer), urea (CH_4N_2O), , sulfur dioxide (SO_2), anthraquinone (AQ) ($C_{14}H_8O_2$), methanol (CH_3OH), ethanol (C_2H_5OH), butanol (C_4H_9OH), formic acid (CH_2O_2), hydrogen peroxide (H_2O_2), acetic acid (CH_3COOH), butyric acid ($C_4H_8O_2$), peroxyformic acid (CH_2O_3), peroxyacetic acid ($C_2H_4O_3$), ammonia (NH_3), tosylic acid (p-TsOH), sodium hypochlorite (NaClO), sodium chlorite ($NaClO_2$), chlorine dioxide (ClO_2), chlorine (Cl_2), or any combination of the above. Exemplary combinations of chemicals for the chemical treatment can include, but are not limited to, NaOH + Na_2SO_3, NaOH + Na_2S, NaOH + urea, NaOH + Na_2SO_3, NaOH + AQ, NaOH + Na_2S + AQ, NaOH + Na_2SO_3 + AQ, Na_2SO_3 + AQ, NaOH + Na_2S + Na_nS (where n is an integer), Na_2SO_3 + NaOH + CH_3OH + AQ, C_2H_5OH + NaOH, CH_3OH + HCOOH, NH_3 + H_2O, and $NaClO_2$ + acetic acid. For example, the first and second chemical solutions can be ≤ 2 wt% NaOH and Na_2SO_3 (e.g., formed by adding H_2SO_3 acid to NaOH).

The chemical treatment can continue (or can be repeated with subsequent solutions) until a desired reduction in lignin content in the plant material piece is achieved. In some aspects, the lignin content can be reduced to between 5% (lignin content is 95% of original lignin content in the natural plant material) and 95% (lignin content is 5% of original lignin content in the natural plant material). In some aspects, the chemical treatment reduces the hemicellulose content at the same time as the lignin content, for example, to the same or lesser extent as the lignin content reduction.

The method 100 can proceed to process block 114, where the treated plant material can be rinsed, for example, with a solvent, such as but not limited to, de-ionized (DI) water, alcohol (e.g., ethanol, methanol, isopropanol, etc.), or any combination thereof. In some aspects, rinsing can be used to remove residual chemicals or particulate(s) resulting from the chemical treatment(s). For example, the partially delignified plant material piece(s) can be partially or fully immersed in one or more rinsing solutions. In some aspects, the rinsing solution can be formed of equal volumes of water and ethanol. In some aspects, the rinsing can be performed without agitation, for example, to avoid disruption of the microstructure. In some aspects, the rinsing may be repeated multiple times (e.g., at least 3 times) using a fresh mixture rinsing solution for each iteration, or until a substantially neutral pH is measured for the chemically-treated plant material piece(s).

If no lignin degradation is instead desired at decision block 104, the method 100 can proceed to process block 116, where the plant material can be infiltrated with water. In some aspects, no lignin degradation may be needed if the starting plant material already has a low lignin content, for example, less than or equal to 15 wt%. The method 100 can then proceed from process block 116 to process block 118, where the hydrated plant material can be heated to an elevated temperature. For example, the plant material can be heated to a temperature greater than about 50° C after infiltration with water.

If no rinsing is desired at decision block 110 or after either of process blocks 114 or 118, the method 100 can proceed to process block 120, where the plant material can be dried to reduce the moisture content of the plant material piece, for example, without removing too much moisture that the plant material piece lose its softened nature (e.g., such that the moisture content is greater than or equal to ~15 wt%). In some aspects, the drying of process block 120 may be effective to reduce a moisture content of the plant material from greater than 30 wt% (e.g., 30-50 wt%) to less than 25 wt%, for example, in a range of 10-20 wt%.

In some aspects, the moisture content of the treated plant material can be reduced to about 10-20% with gentle drying conditions prior to subsequent treatment steps. For example, drying can be accomplished by use of a kiln. Alternatively, drying can be accomplished by placing the treated plant material into a chamber and subsequently reducing the pressure within the chamber. In some aspects, the treated plant material can be restrained in a manner that prevents dimensional distortion during the drying process. For example, the treated plant material can be sandwiched between metal screens and dried at low pressure in a hot press, so as to restrain the plant material to prevent or at least reduce dimensional distortion while effectively drying the material. In some aspects, drying of the treated plant material can facilitate absorption of the stabilizing agent and/or precursors in the subsequent treatment step.

Alternatively or additionally, the drying of process block 120 can include any of conductive, convective, and/or radiative heating processes, including but not limited to an air-drying process, a vacuum-assisted drying process, an oven drying process, a freeze-drying process, a critical point drying process, a microwave drying process, or any combination of the above. For example, an air-drying process can include allowing the processed plant material piece(s) to naturally dry in static or moving air, which air may be at any temperature, such as room temperature (e.g., 23° C) or at an elevated temperature (e.g., greater than 23°C). For example, a vacuum-assisted drying process can include subjecting the processed plant material piece(s) to reduced pressure, e.g., less than 0.1 MPa, for example, in a vacuum chamber or vacuum oven. For example, an oven drying process can include using an oven, hot plate, or other conductive, convective, or radiative heating apparatus to heat the processed plant material piece(s) at an elevated temperature (e.g., greater than 23° C), for example, 70° C or greater. For example, a freeze-drying process can include reducing a temperature of the processed plant material piece(s) to below a freezing point of the fluid therein (e.g., less than 0° C), then reducing a pressure to allow the frozen fluid therein to sublime (e.g., less than a few millibars). For example, a critical point drying process can include immersing the processed plant material piece(s) in a fluid (e.g., liquid carbon dioxide), increasing a temperature and pressure of the plant material piece(s) past a critical point of the fluid (e.g., 7.39 MPa, 31.1° C for carbon dioxide), and then gradually releasing the pressure to remove the now gaseous fluid. For example, a microwave drying process can include using a microwave oven or other microwave generating apparatus to induce dielectric heating within the processed plant material piece(s) by exposing it to electromagnetic radiation having a frequency in the microwave regime (e.g., 300 MHz to 300 GHz), for example, a frequency of ~915 MHz or ~2.45 GHz.

The method 100 can proceed to process block 122, where the plant material can be infiltrated with a solution of water blocking agent precursors and/or water blocking agent. In some aspects, the water blocking agent can be and/or comprise one or more hydrophilic reactive monomers. For example, the water blocking agent precursors can comprise a nucleophile and an electrophile, and the water blocking agent can comprise a reaction product of the nucleophile and the electrophile. Each of the water blocking agent precursors can have a molecular weight less than or equal to 500 g/mole, such that, during the infiltrating, the water blocking agent precursors become absorbed within amorphous cellulose and hemicellulose regions of cell walls of the plant material. Alternatively or additionally, in some aspects, where the solution infiltrated into the plant material during process block 122 comprises the water blocking agent, the water blocking agent can also have a molecular weight less than or equal to 500 gm/mole, such that, during the infiltrating, the water blocking agent becomes absorbed within amorphous cellulose and hemicellulose regions of cell walls of the plant material. In some aspects, the nucleophile comprises an aromatic nucleophile (e.g., phenol or cresol) and the electrophile comprises an aldehyde (e.g., formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, or glutaraldehyde), an oxirane, an oxazolidine, or a bisoxazolidine.

In some aspects, the nucleophile is phenol, the electrophile is formaldehyde, and the water blocking agent is methylolated phenol. For example, in some aspects, the water blocking agent precursors can comprise an aqueous solution with a viscosity that is less than about 40 cPs (20 °C). In some aspects, the solution comprises water as the solvent, and solute molecules that are dissolved in the water. In some aspects, all (or at least 90%) of the solute molecules in the solution have molecular weight values that are less than 500 g/mole. In some aspects, all (or at least 90%) of the solute molecules in the solution have molecular weight values that are less than 300 g/mole. In some aspects, all (or at least 90%) of the solute molecules are even smaller, for example, less than 150 g/mole.

The combination of both low solution viscosity and very low solute molecular weight can provide certain advantages over conventional water stabilization processes. For example, larger solute molecules are not capable of diffusing into the specific regions of plant material tissue that have the greatest affinity for water molecules, and the regions that are responsible for most of the swelling when water is absorbed into plant material. Such regions include amorphous cellulose and amorphous hemicellulose. Alternatively or additionally, the water blocking agent can be highly soluble in water, which can promote spontaneous transfer of these compounds to the amorphous cellulose and hemicellulose regions of the cell wall during the infiltration process.

In some aspects of the disclosure, the water blocking agent is highly hydrophilic. In some aspects, the water blocking agent can be water soluble, under alkaline conditions, neutral conditions, or both. In certain aspects, the water blocking agent has a water solubility value that is greater than or equal to 2 g of dissolved compound per 100 mL of water at a temperature of 20 °C, such as greater than or equal to 5 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 10 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 15 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to than 20 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 25 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 30 g of dissolved compound per 100 mL of water at a temperature of 20 °C. In some aspects of the disclosure, the water blocking agent has a high water solubility value that is greater than or equal to 30 g of dissolved compound per 100 mL of water at a temperature of 20 °C.

As used herein, the term “dissolved solute” is not intended to include “dispersed compound”, “suspended compound”, or “emulsified compound”. The latter compositions would generally not be capable of diffusing to the amorphous cellulose and hemicellulose regions in the plant cell walls. Thus, crosslinking of the amorphous cellulose and hemicellulose regions in the plant cell walls could not be achieved by employing dispersed, suspended, or emulsified compounds.

In some aspects, the water blocking agent has the potential to crosslink the plant material tissue (amorphous cellulose and hemicellulose). The selection of the water blocking agent is such that the crosslinking reaction does not occur rapidly at low temperature (e.g., 20-50° C). Rather, the crosslinking reaction occurs relatively slowly at elevated temperatures (e.g., ≥130° C). This set of reaction rate characteristics can facilitate a process in which plant material can first be consolidated (e.g., densified via compression) at elevated temperature (e.g., about 130° C), and can then be crosslinked at an even higher temperatures (e.g., ≥ 150° C). Amorphous cellulose and hemicellulose that have been effectively crosslinked will have some capacity to absorb water, but will be very limited in their ability to undergo volumetric expansion.

In some aspects, the water blocking agent precursors can be (i) mixtures of nucleophiles and electrophiles, (ii) reaction products of nucleophiles and electrophiles, (iii) or mixtures of nucleophiles, electrophiles and reaction products. At the time of infiltration, the molecular weight of each of the electrophiles, nucleophiles, and reaction products, independently, can be less than 500 g/mole, for example, from greater than 0 g/mole to a molecular weight less than 500 g/mole, or from greater than 0 g/mole to less than 300 g/mole, or from greater than 0 g/mole to 150 g/mole. Techniques for verifying the solute molecules are all of low molecular weight include, but are not limited to, gel electrophoresis, gel permeation chromatography, and mass spectroscopy.

In some aspects of the disclosure, the water blocking agent precursors are highly hydrophilic. In particular aspects disclosed herein, the water blocking agent precursors can be water soluble, under alkaline conditions, neutral conditions, or both. In certain aspects, the stabilizing agent precursors have a water solubility that is greater than or equal to 2 g of dissolved compound per 100 mL of water at a temperature of 20 °C, such as greater than or equal to 5 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 10 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 15 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to than 20 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 25 g of dissolved compound per 100 mL of water at a temperature of 20 °C, or greater than or equal to 30 g of dissolved compound per 100 mL of water at a temperature of 20 °C. In some aspects of the disclosure, the water blocking agent precursors have a high water solubility value that is greater than or equal to 30 g of dissolved compound per 100 mL of water at a temperature of 20 °C.

In some aspects, nucleophiles can include aromatic nucleophiles, such as phenol, cresol, aniline, resorcinol, aminophenol, and metaphenylenediamine. Alternatively or additionally, the nucleophiles can include nucleophiles that are not aromatic, such as urea and morpholine. For some of these nucleophiles, the pH of the stabilizing agent solution can be adjusted to achieve the required level of water solubility.

In some aspects, electrophiles can include aldehydes, oxiranes, and oxazolidines, including bisoxazolidines. Aldehydes can include formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, acrolein, and glutaraldehyde. Oxazolidines and bisoxazolidines can yield stabilizing agents with lower levels of volatility. An example of a suitable bisoxazolidine is hydroxymethyl dioxoazabicyclooctane, with a molecular weight of 145 g/mole.

In some aspects, water blocking agents can include low-molecular-weight reaction products obtained by reacting the aforementioned nucleophiles and electrophiles. Examples of suitable adducts can include methylolated phenol, with a molecular weight of 124 g/mole, or methylolated cresol, with a molecular weight of 138 g/mole.

In some aspects, water blocking agent precursor solutions can be prepared by combining nucleophiles, electrophiles, and water together in a mixing vessel. The resulting solution can then be used as a water blocking agent precursor solution. The ratio of nucleophile to electrophile can be about 1:0.9 to 1:3 on a molar basis (e.g., 1 mole of nucleophile to 2 moles of electrophile). In some aspects, the water blocking agent can comprise more than one nucleophile and/or more than one electrophile. The water content of the solution containing water blocking agent precursors and/or water blocking agent can be in a range of 20-95%, inclusive. In some aspects, the water content can have a substantial impact on the level of active solute that is loaded into the plant material during the infiltration process, for example, when the stabilizing agent is incorporated into the plant material by use of a soaking process. In this type of process, lower water content values can result in higher levels of solute in the plant material.

In some aspects, water blocking agents can be prepared by reacting nucleophiles and electrophiles together to form low-molecular-weight adducts. For example, methylolated phenol can be prepared by reacting phenol with formaldehyde in an aqueous medium. A mixing tank that has been equipped with a heating and cooling system can be charged with phenol and optionally, water, sodium hydroxide, and/or a catalyst. In some aspects, sodium carbonate can be used as a catalyst and can be added at a level of about 0.0001-0.01% of the mass of the phenol in the initial stages of the manufacturing process. With continuous stirring, formaldehyde can be added to the mix tank at a specific rate or in discreet charges over a period of time. In some aspects, the formaldehyde can be in the form of formalin, such as a 50% formalin solution. In some aspects, the formaldehyde can be in the form of paraformaldehyde. The formaldehyde can be added at a slow rate to help ensure that the mixture does not over-heat as exothermic reactions between the phenol and formaldehyde occur. In some aspects, the temperature of the mixture can be maintained in the range of about 50-80° C during this process. The molar ratio of formaldehyde to phenol can be about 3.0-1.0. The water level in the mixture can be about 30-80%. The sodium hydroxide level (solids content) can be about 1-15% of the phenol charge (mass/mass basis). In some aspects, the phenol can be replaced with cresol (e.g., meta-cresol) or other substituted phenol compounds.

In some aspects, it can be desirable to use a sodium hydroxide level of 0.1-3.0% of the mass of the phenol charge until nearly all of the formaldehyde has reacted with the phenol. This approach helps to avoid disproportionation of the formaldehyde, which tends to happen at pH values that are greater than about 9. Upon complete addition of all of the formaldehyde, the mixture can be stirred and heated such that the temperature of the mixture is maintained in the range of about 60-90° C for a period of about 1-2 hours. During this process, the viscosity of the mixture can be assessed by use of Garnder-Holdt bubble tubes or other methods of viscosity measurement. Reactions in the mixture can be quickly inhibited by cooling the mixture to a temperature of about 20 °C if the viscosity increases to a value greater than about 40 cPs.

In some aspects, all of the formaldehyde and phenol are consumed in this process and form monomeric methylolated phenol with no oligomer formation. Alternatively, in some aspects, a modest level of oligomer formation can also occur in the reaction mixture. Oligomers can be comprised of two or three substituted phenol groups that are bonded together through ether linkages. Oligomer formation, especially trimers and larger oligomers, can limit the ability of the mixture to absorb into the plant cell wall. Thus, oligomer formation should be avoided. Reaction schedules that achieve nearly complete consumption of phenol and formaldehyde with minimal oligomer formation can be empirically optimized by subjecting reaction mixtures after different reaction periods to mass spectroscopy or gel permeation chromatography in order to assess the reaction product distribution.

In some aspects, urea can be added to the mixture at the later stages of the production process (e.g., either after cooling or just prior to cooling) to reduce the emission of residual formaldehyde that might exist in the mixture. In some aspects, additional sodium hydroxide can be added to the mixture at the later stages of the production process in order to improve the phase stability. In some aspects, the sodium hydroxide level in the formulation can be low or it can be completely omitted from the formula. In some aspects, the resulting mixture can be used directly as a water blocking agent. In other aspects, the resulting mixture can be further formulated with water, nucleophile(s), or electrophile(s) to obtain the water blocking agent treatment solution.

In some aspects, a high percentage of the phenol-based molecules in the methylolated phenol composition can exist as a single phenol molecule with about 1-3 methylol groups attached at the ortho and para positions of the phenol ring. These compounds are exceptionally good at absorbing into plant tissue, especially the regions of the cell wall based on amorphous cellulose and hemicellulose. For example, such compounds can have a molecular weight in a range of about 124-184 Daltons, inclusive. In some aspects, oligomers comprising about 2-3 methylolated phenol compounds that have condensed together can also absorb into plant tissue, including the regions of the cell wall based on amorphous cellulose and hemicellulose. Although the oligomers may absorb into the plant material tissue at a rate that is slower than that of the monomeric methylolated phenol compounds, the small oligomers can have the benefit of having a lower vapor pressure than the methylolated phenol monomer, which can improve health and safety aspects of the manufacturing process.

Compositions comprising higher molecular weight condensates of the methylolated phenol compounds, such as compositions that would typically be used as bonding resins for plywood, oriented strandboard, or other wood composites, tend to absorb into cracks and vessels on the surface of the plant material, but do not generally absorb into the cell wall of the plant material tissue. A commercial example of higher molecular weight condensates of the methylolated phenol compounds has the trade name 70CR66 phenolic bonding resin (manufactured by Bakelite Synthetics in Atlanta, Georgia). Higher molecular weight phenolic resins, which are commonly used as wood adhesives, and include compositions such as 70CR66, do not yield the desired product or performance attributes, and are not suitable for use according to contemplated aspects of the disclosed subject matter. The average molecular weight of the molecules in these phenolic resins can be about 1,500-5,000 Daltons. In some aspects, about 95% of the solids mass of the water blocking agent has a molecular weight less than about 200 Daltons.

In some aspects, one or more sections of treated plant material can be immersed in an aqueous solution with water blocking agent and/or water blocking agent precursors. The system (e.g., the solutions with added sections of treated plant material) can be subjected to one or more vacuum cycles to help facilitate absorption of the solution into the specific targeted regions of the plant tissue. Alternatively, the system can be subjected to increased pressure (e.g., using a pressure vessel) in order to help facilitate absorption of the solution into the plant material. For example, the system could be subjected to a pressure of about 3-15 bar, inclusive.

In some aspects, the absorption process can be continued for a period of time that is sufficient to achieve distribution of the water blocking agent (and/or precursors thereof) throughout the entire cross-section of the treated plant material. The soaking time required to achieve absorption of the water blocking agent and/or precursors thereof through the entire cross-section of the plant material can be dependent upon multiple factors, including the thickness and width dimensions of the plant material, the specific formulation of the water blocking agent and/or water blocking agent precursors, the temperature, and the amount of pressure applied to the system. As an example, sections of lumber having a thickness of 17 mm, a width of 180 mm, and a length of 244 cm can require a soak time of about 3 hours when the temperature is 25° C and the gauge pressure is 725 MPa for methylolated phenol as the water blocking agent.

During the water blocking agent soaking process, the moisture content of the treated plant material can be increased from a first moisture content of about 1-20% to a second moisture content of about 5-35%. The amount of absorbed water blocking agent solute or absorbed water blocking agent precursor solute can be about 1-200% of the dry mass of the plant material. In some aspects, the water blocking agent loading process can occur at a temperature of about 20 °C. Alternatively, in some aspects, the water blocking agent loading process can occur at an elevated temperature, such as 30-50 °C.

In some aspects, the methylolated phenol can be selectively absorbed in amorphous cellulose and/or the amorphous hemicellulose portions of the cell wall throughout the cross-section of the treated lignocellulosic material by the end of this process. In some examples, distribution of methylolated phenol in the plant material can be facilitated by use of sections of treated plant material that have a thickness less than about 6.4 mm (0.25 inches). In some aspects, using increased pressure and slightly elevated temperature can also improve the initial distribution of the methylolated phenol in cell walls throughout the complete cross section of the treated plant material. In some aspects, methylolated phenol with a relatively low molar ratio of formaldehyde to phenol, such as a molar ratio of about 1:1 to 1.5:1, can be used in order to help retard cure rate during subsequent processing steps (e.g., drying, compressing, etc.). Premature curing of the methylolated phenol can result in failure to achieve a desired high-density value in the treated, infiltrated, and compressed plant material product.

Although the above description focuses on methylolated phenol as the water blocking agent, aspects of the disclosed subject matter are not limited thereto. Rather, in some aspects, other hydrophilic reactive monomers can be used in the water blocking agent to similar advantage, such as but not limited to methylolated cresol, methylolated substituted phenol, or combinations thereof (with or without methylolated phenol). Alternatively, in some aspects, the water blocking agent can be and/or comprise a hydrophobic reactive monomer, a wax, a sizing agent, a drying oil, a topical sealant, or other material(s) that inhibit, or at least reduce, water absorption in plant materials.

The method 100 can proceed to decision block 124, where it is determined if the plant material infiltrated with the solution of water blocking agent precursors or water blocking agent should be dried. If drying is desired, the method 100 can proceed to process block 126, where the plant material is dried, for example, in a manner similar to that described above for process block 120. For example, the treated and infiltrated plant material can be dried to a moisture content of about 1-25% prior to subsequent treatment steps. In some aspects, this drying step can be conducted in a manner that does not cause the absorbed solute of the water blocking agent to prematurely crosslink the amorphous cellulose or hemicellulose before the plant material has been compressed to the targeted level. Appropriate drying conditions will be dependent upon the specific water blocking agent composition or water blocking agent precursor composition and the dimensions of the plant material. In some aspects, the treated and infiltrated plant material can be dried at a temperature in range of 40-100 °C (e.g., about 60-80° C for a period of about 6-10 hours). In some aspects that utilize higher temperatures from the selected range, the treatment time may be accordingly reduced, so as to reduce the risk of prematurely curing the loaded water blocking agent.

In some aspects, drying can be accomplished in a chamber that operates under reduced pressure, which can allow for more efficient removal of water at lower temperatures. This can help to ensure that the water blocking agent does not prematurely cure during the drying step. In some examples, the treated and infiltrated plant material can be mechanically restrained in a manner that prevents dimensional distortion during the drying process. In some aspects, a moisture content of about 15-25% may be helpful for subsequent compression steps. In some aspects, it may further be advantageous that the drying process is conducted in a manner that does not result in curing of the absorbed water blocking agent compounds at this stage of the process.

Drying the plant material for this period of time without crosslinking the amorphous cellulose and hemicellulose can be achieved by selection of a water blocking agent with a relatively high energy of activation value. For example, water blocking agent formulations based on less reactive nucleophiles, such as phenol and cresol, can help to achieve this condition. Alternatively or additionally, in some aspects, faster drying rates can be facilitated without the risk of premature crosslinking by conducting the drying process under reduced pressure. Devices suitable for conducting the drying process can include, but are not limited to ovens, kilns, and drying presses. In some aspects, the treated (lignin degraded) and infiltrated plant material can be mechanically restrained in a manner that prevents dimensional distortion during the drying process. Subsequent to the drying process, the treated and infiltrated plant material can have a moisture content value in the range of about 1-25%.

After the drying of process block 126, or if no drying was desired at decision block 124, the method 100 can proceed to decision block 128, where it is determined if a partial compression (e.g., partial densification) is desired. If partial compression is desired, the method 100 can proceed to process block 130, where the plant material is compressed (e.g., along at least its thickness direction) to have a first density of at least 900 kg/m^3, for example, in a range of 900-1200 kg/m^3. In some aspects, the compression of process block 130 is controlled to avoid premature crosslinking of any (or at least most, e.g., 90%) of the amorphous cellulose or hemicellulose by action of the water blocking agent and/or precursors thereof within the plant material.

In some aspects, the plant material can be pressed in a direction crossing its fiber direction. Alternatively, in some aspects, the pressing can be in a direction substantially perpendicular to the fiber direction, while in other aspects, the pressing may have a force component perpendicular to the fiber direction. In any event, the partial compression of process block 128 can be effective to reduce a thickness of the plant material, thereby increasing its density as well as collapsing (at least partially) the natural lumina (e.g., vessels, lumen in each fiber, parenchyma cells, etc.), voids, and/or gaps within the cross-section of the plant material. In some aspects, the pressing can be along a single direction (e.g., along radial direction R), for example, to reduce a thickness of the lignin-compromised plant material piece(s) (e.g., at least a 50% reduction in dimension as compared to the plant material piece(s) prior to pressing). Alternatively or additionally, in some aspects, the plant material piece(s) can be simultaneously pressed in two orthogonal directions (e.g., both perpendicular to the fiber direction), for example, to reduce a cross-sectional area of the plant material piece(s) (e.g., to produce a densified rectangular strip). Alternatively or additionally, in some aspects, the plant material piece(s) can be sequentially pressed in different orthogonal directions.

In some aspects, the pressing may be performed without any prior drying of the plant material piece(s) or with the plant material piece(s) retaining at least some water or other fluid therein. The pressure and duration of the pressing can be a factor of the size of plant material piece(s) prior to pressing, the desired size of the plant material piece(s) after pressing, the water or fluid content within the plant material piece(s) (if any), the temperature at which the pressing is performed, relative humidity, and/or other factors. For example, the plant material piece(s) can be held under pressure for a time period of 1 minute up to several hours (e.g., 1-180 minutes, inclusive). In some aspects, the plant material piece(s) can be held under pressure for 3-72 hours, inclusive. In some aspects, the pressing can be performed at a pressure between 0.5 MPa and 20 MPa, inclusive, for example, 5 MPa. In some aspects, the pressing may be performed without heating (e.g., cold pressing), while in other aspects, the pressing may be performed with heating (e.g., hot pressing). For example, the pressing may be performed at a temperature between 20 ºC and about 160 ºC, e.g., greater than or equal to 100 ºC. When the plant material is being pressed at relatively high temperatures (e.g. 160° C), the duration of the pressing process can be sufficiently short such that the infiltrated water blocking agent does not prematurely crosslink the amorphous cellulose and/or hemicellulose in the plant material cell wall. In some aspects, the pressing can be effective to fully collapse the lumina of the native cellulose-based microstructure of the plant material and/or can result in a density for the compressed plant material of at least 0.9 g/cm^3 (e.g., $\geq$ 1.1 g/cm^3 or $\geq$ 1.2 g/cm^3, for example, in a range of 1.3-1.5 g/cm^3).

For example, the treated, infiltrated, and dried plant material can be loaded into a press wherein the top and bottom platens of the press have a temperature in the range of about 20-120 °C. The treated, infiltrated, and dried plant material can be oriented in the press such that the thickness axis of the plant material is orthogonal to the contacting surface of the platens. The pressure applied to the treated, infiltrated, and dried plant material can be increased from 0 to about 3-8 MPa over a period of 0-10 minutes. The applied pressure can then be sustained until the treated, infiltrated and dried plant material has been compressed to about 40-60% of the original thickness. The density of the treated, infiltrated, and dried plant material at this point can be about 900-1250 kg/m^3. This compression process can take about 5-100 minutes depending on the original thickness of the plant material, the applied pressure, the temperature of the platens, the species of plant material, and other factors including those related to the lignin degradation.

Upon achieving the desired level of compression, the pressure applied to the compressed plant material can then be relieved, and the compressed plant material can thereafter be removed from the press. As noted above, the partial compression can be such that, after removal from the press, the absorbed water blocking agent solute molecules do not prematurely crosslink the amorphous cellulose or hemicellulose in the plant material. Alternatively or additionally, in some aspects, the treated, infiltrated, and dried plant material can be partially compressed in a first compression step, such that the density of the compressed plant material is about 900-1250 kg/m^3, the moisture content is greater than about 10%, and the absorbed water blocking agent solute molecules (or precursors thereof) do not crosslink the amorphous cellulose and hemicellulose. In some aspects, it can be beneficial for the temperature of the platens to be in the range of about 20-60 °C for the compression of process block 130, which lower temperature can help ensure that the absorbed water blocking agent (e.g., methylolated phenol) does not cure during the compression. In some aspects, compression at these lower temperature values can be facilitated by partial degradation of the lignin (and/or hemicellulose) during process block 106, 112, or 118, for example, due to thermal exposure of the lignin and/or the hemicellulose.

After the partial compression of process block 130, or if no partial compression was desired at decision block 128, the method can proceed to decision block 132, where it is determined if drying is desired. If drying is desired, the method 100 can proceed to process block 134, where the plant material is dried, for example, in a manner similar to that described above for process block 120. For example, the partially compressed plant material can be subjected to an additional drying step where the moisture content of the plant material is reduced to less than about 10%, from example, in a range of 1-10%, inclusive. In some aspects, drying can be accomplished by use of a kiln or oven. Alternatively, drying can be accomplished in a chamber that operates under reduced pressure. In some aspects, the treated, infiltrated, and partially compressed plant material can be restrained in a manner that prevents dimensional distortion (warping or twisting) during the drying process. Drying under reduced pressure at low temperature can be helpful to ensure that the absorbed water block agent (or precursors thereof) does not prematurely crosslink the amorphous cellulose and hemicellulose during the drying.

After the drying of process block 134, or if no drying was desired at decision block 132, the method 100 can proceed to decision block 136, where it is determined if full compression (e.g., complete densification) is desired. If full compression is desired, the method 100 can proceed to process block 138, where the plant material is compressed (e.g., along at least its thickness direction) to have a second density greater than the first density. For example, the second density can be at least 1200 kg/m^3, for example, in a range of 1250-1450 kg/m^3. In some aspects, the compression of process block 138 may be performed in a similar manner to that described above for process block 130. In some aspects, the dry plant material from process block 134 can then be subjected to a final hot-pressing step, where the density of the plant material is increased to a value in the range of about 1200-1450 kg/m^3, inclusive. Subsequent to achieving the targeted level of compression, the absorbed stabilizing agent solute molecules can crosslink the amorphous cellulose and hemicellulose in a manner that significantly prevents them from undergoing volumetric expansion in the presence of water, or at least reduces their rate of volumetric expansion.

For example, the treated, infiltrated, partially-compressed, and dried plant material can be loaded into a press wherein the top and bottom platens of the press have a temperature in the range of about 20-200 °C, inclusive (e.g., 20-150 °C). The plant material can be oriented in the press such that the thickness axis of the plant material is orthogonal to the contacting surface of the platens. The pressure applied to the treated, infiltrated, partially compressed, and dried plant material can be increased from 0 to about 3-10 MPa over a period of 0-10 minutes. The applied pressure can then be sustained until the treated, infiltrated, partially compressed, and dried plant material has been compressed to a level that corresponds to a density of about 1200-1450 kg/m^3. Alternatively or additionally, in some aspects, the density of the treated, infiltrated, partially compressed, and dried plant material can be increased to a value that is greater than about 1300 kg/m^3, for example, at least 1350 kg/m^3. In some aspects, the full compression process can take about 2-40 minutes depending on the original thickness of the plant material, the applied pressure, the temperature of the platens, the plant material species, and other factors (e.g., those related to the partial compression of process block 130).

In some aspects, only a single compression step is used in the fabrication process (e.g., only process block 138 without prior compressing via process block 130). In such aspects, the pressure and associated time of the compressing (e.g., hot-pressing) can be selected to yield the desired level of compression, and the elevated temperature and associated time can be selected to crosslink the amorphous cellulose and hemicellulose (and optionally the lignin) once the targeted level of compression has occurred. In some aspects, the single-step full compression can be performed on treated, infiltrated and dried plant material having a moisture content that is less than about 12%.

In some aspects, the compression of process block 138 can be controlled to avoid crosslinking of the amorphous cellulose and hemicellulose prior to achieving the desired level of compression. In such aspects, after process block 138, the method 100 can proceed to process block 140, where the amorphous cellulose and hemicellulose are crosslinked with water blocking agent within the plant material. For example, after complete compression of the plant material has been achieved, the amorphous cellulose and hemicellulose can be crosslinked via the water blocking agent such that they are not able to undergo significant levels of volumetric expansion in the presence of water, or at least such that the rate of volumetric expansion due to water exposure is reduced. In some aspects, after achieving the targeted level of compression, the plant material can be further heated until crosslinking of the amorphous cellulose and hemicellulose have occurred. Alternatively or additionally, crosslinking of degraded lignin can also occur at this step in the process. For example, degraded lignin within the highly compressed plant material can be crosslinked such that the previously degraded lignin is no longer soluble in water. Alternatively, in some aspects, the amorphous cellulose and hemicellulose can be crosslinked during at least part of process block 138 (e.g., before the pressure on the plant material has been relieved in the press).

For example, the treated, infiltrated, partially compressed, and dried plant material can be fully compressed to a density in a range of about 1200-1450 kg/m^3 in process block 138 and the treated, infiltrated, dried, and fully compressed plant material can be removed from the press and transferred to a kiln in order to crosslink the amorphous cellulose, hemicellulose and degraded lignin at process block 140. In some aspects, the plant material can be restrained during further heating in order to prevent, or at least reduce, the formation of geometric defects, such as twist or warpage. For example, after complete compression of the plant material has been achieved, the water blocking agent compounds in the treated, infiltrated, and compressed wood can be cured or otherwise converted into a polymerized state such that they are not soluble in water. In some examples, the water blocking agent compounds can be cured by exposure to an elevated temperature ranging from about 50 °C to about 250 °C. In some aspects, the exposure to the elevated temperature can last for about 1-200 minutes.

After crosslinking, the method 100 can proceed to process block 142, where the water-stabilized, densified plant material can processed for subsequent use and/or used (e.g., for reinforcing concrete and/or cement). In some aspects, the processing of process block 142 can include mechanically processing the densified plant material into individual lignocellulosic fibers. For example, the plant material can be subjected to cutting, slicing, stamping, molding, warping, or any other plant material processing technique. In some aspects, the use of process block 142 can include combining, mixing, or otherwise providing the individual lignocellulosic fibers to concrete or cement, to act as a reinforcing component thereof. In some aspects, the lignocellulosic fibers can be mixed with wet concrete or cement (or components thereof), and the mixture set to form a rigid composite structure with lignocellulosic fibers embedded therein (e.g., in a random arrangement), wherein most of the water that was mixed with the cement or concrete has reacted with the metal oxide particles, such as calcium oxide, to form an intractable, inorganic matrix. Thus, after a short period of time, most of the water that is initially present in a slurry of cement and water, is no longer available to absorb into the modified fibers.

In some aspects, the plant material is processed into individual lignocellulosic fibers after the water blocking agent has cured (e.g., after process block 140). Alternatively, in some aspects, the plant material is processed into individual lignocellulosic fibers before the water blocking agent has fully cured (e.g., prior to or during process block 140), for example, while the plant material is still relatively soft. In such aspects, the lignocellulosic fibers can then be subjected to heat treatment (e.g., process block 140) to cure the water blocking agent therein, thereby further setting the shape of the fibers. In some aspects, the compressed fibers can be subject to the aqueous solution for a limited period of time in order to achieve the dog-bone shape in the fibers, as exposing the compressed fibers to an aqueous solution for an unlimited or extended period of time may result in swelling of the fiber along its entire length.

In some aspects, sections of the plant material can be sliced or cut along the longitudinal axis (e.g., L in FIG. 2) to yield a plurality filaments with a width and thickness in a cross-section that is less than or equal to 5 mm, and these filaments can be accumulated in oriented bundles and chopped to yield individual lignocellulosic fibers that have a length less than or equal to 150 mm. In some aspects, the width and thickness of each fiber can be at least an order of magnitude less than (e.g., no more than 10% of) a length of the respective fiber. In some aspects, sections of the plant material can be cut along the width axis to yield wide sections with a length less than or equal to 150 mm. These sections can be loaded into special trays or cartridges that feed the sections into knives or other cutting tools, which can rapidly convert the sections into individual lignocellulosic fibers having a width of less than 5 mm and a length less than 150 mm.

For example, each lignocellulosic fiber 300 can have a thickness, t, in a cross-sectional plane perpendicular to a direction of extension 302 of the fiber 300 that is less than or equal to 5 mm (e.g., 0.5-5 mm, inclusive), as shown in FIG. 3A. In some aspects, each lignocellulosic fiber 300 can have a length, l, along the direction of extension 302 that is greater than 10 mm (e.g., 10-150 mm, inclusive). In some aspects, the direction of extension 302 may be substantially parallel to an axial direction (e.g., L in FIG. 2) of the plant material, and/or the thickness direction 304 may be substantially parallel to a radial direction (e.g., R in FIG. 2) or a tangential direction (e.g., T in FIG. 2) of the plant material. In some aspects, the thickness direction 304 can correspond to a direction of compression in process block 130 and/or process block 138. In some aspects, the plant material (e.g., from process block 138) that is mechanically processed into separate lignocellulosic fibers can have thickness, width, and/or length dimensions much greater than that of the resulting fibers. For example, the length of the plant material can be up to about 245 cm (about 8 ft), and/or the width of the plant material can be up to about 122 cm (about 4 ft). Alternatively, in some aspects, the plant material can have a length and/or width in a range of about 2.5-510 cm, inclusive (about 1-200 inches).

In some aspects, each lignocellulosic fiber 300 can have a width, w, in the cross-sectional plane perpendicular to the direction of extension 302 that is the same or substantially similar (e.g., within 10%) of the dimension of the thickness, t, for example, such that the cross-section is substantially square. Alternatively or additionally, in some aspects, the lignocellulosic fibers can be formed to have a complex shape (e.g., non-rectangular in side view), such as but not limited to a zig-zag pattern, a sinusoidal pattern, or a dog-bone shape. For example, sections of the plant material can be formed into individual lignocellulosic fibers with the complex shape (or any other shape) via slicing or cutting by one or more knives, via a laser cutting tool, or via any other mechanical process. In some aspects, the plant material may first be cut into individual filaments having the complex shape, and then accumulated into oriented bundles and chopped to yield the lignocellulosic fibers having a shorter length (e.g., in a range of 10-150 mm, inclusive). Alternatively, in some aspects, the lignocellulosic fibers can be formed to have the complex shape via warping, for example, by exposing to high heat (e.g., > 50 °C) on one side. For example, the plant material can be cut into individual filaments having a non-complex shape (e.g., rectangular shape in side view), and the filaments can be exposed to high heat on one side to induce a complex shape (e.g., curved or arcuate, such as a sinusoid) via warping. The warped filaments can then be chopped into individual lignocellulosic fibers reflecting the complex shape.

Other techniques for forming the plant material into individual lignocellulosic fibers are also possible according to one or more contemplated aspects. For example, blocks of plant material can be subjected to two-dimensional slicing or sawing to convert each block into an article with a multitude of hanging filaments on one end (e.g., similar to a broom). The filaments on the converted block can then be removed by cutting, for example, to generate a plurality of separate lignocellulosic fibers. In another example, the lignocellulosic fibers can be formed from the plant material by stamping with a cutting or punch tool. In some aspects, the punch tool can yield rectangular shaped fibers or fibers having a complex shape.

In some aspects, a complex shape can be induced in the individual lignocellulosic fibers by taking advantage of the swell potential of the densified plant material, which swell potential may be greater than non-densified plant materials. For example, FIG. 1B shows a simplified method 150 for forming lignocellulosic fibers with a dog-bone shape using swelling induced by water exposure. At process block 152, one or more lignocellulosic fibers can be exposed to an aqueous environment such that water infiltrates into the fibers. In some aspects, the water can preferentially infiltrate into the fibers via axial ends thereof (e.g., opposite ends along a direction of extension 302), for example, due to the orientation of the fiber with respect to the microstructure of the underlying plant material (e.g., the direction of extension 302 being aligned with the axial direction L of the starting plant material) and/or cutting planes defining the axial ends (e.g., substantially perpendicular to axial direction L of the starting plant material). The water infiltration can cause the fiber to swell along its thickness direction, starting at the axial ends and moving inward. In some aspects, the exposure to the aqueous environment can continue until the desired dog-bone shape for the lignocellulosic fiber has been achieved, as determined at decision block 154, after which the exposure of the lignocellulosic fiber to the aqueous environment can cease at process block 156.

In some aspects, the swelling of the fibers to have the dog-bone shape may occur prior to curing of the water blocking agent therein. For example, the exposure of process block 152 can be (i) after the compression of process block 130 but prior to the compression of process block 138 or (ii) after the compression of process block 138 but prior to the curing of process block 140. After the dog-bone shape is achieved and the exposure to the aqueous environment is ceased, the water blocking agent in the fiber can optionally be cured at process block 158 (e.g., via process block 140 or similar heat treatment), for example, to set, or at least further stabilize, the dog-bone shape of the fiber.

For example, the aqueous environment can be an aqueous solution with the water blocking agent (or precursors thereof) therein. In some aspects, a lignin-degraded plant material 312 can be subjected to densification 310 (e.g., process blocks 130 and/or 138 in FIG. 1A) to reduce its thickness from an initial value, t1, to a reduced value, t2, as shown schematically in FIG. 3B. After densification, the plant material having the reduced thickness, t2, can be mechanically processed 316 into individual fibers, which is then immersed 318 into an aqueous solution 320 with water blocking agent therein. During the immersion 318, the densified fibers 314 will absorb a portion of the aqueous solution, which absorption may be non-uniform. Instead, the absorption may disproportionately occur at the ends 314a, 314b of the fiber 314, which ends 314a, 314b absorb fluid at a rate that is faster than that of the middle. Without being bound by any particular theory, it is believed that the end 314a, 314b absorb at a faster rate in some aspects since they have more surface area as well as exposed end grain. As the lignocellulosic fiber ends 314a, 314b absorb greater amounts of the fluid, they will swell more than the rest of the fiber 314, which non-uniform swelling will result in fibers with a dog-bone shape 322. Specifically, the resulting lignocellulosic fiber 324 will have thickness values (e.g., a maximum thickness, t4, equal to or approaching the thickness, t1, of the original plant material 312) at the fiber ends 326a, 326b that are larger than the thickness values in the middle 328 of the fiber 324 (e.g., a minimum thickness, t3, equal to or approaching the thickness, t2, of the densified fiber prior to aqueous exposure).

When sufficient time has elapsed to achieve the desired non-uniform swelling of the lignocellulosic fiber, the aqueous solution can be separated from the fiber, for example, by subjecting the suspension to a screen or by some other rapid separation method. For example, rectangular-shaped lignocellulosic fibers can be submerged into an aqueous solution of methylolated phenol for a period of 1-30 minutes, inclusive, at a temperature of 20-60 °C, inclusive. Within a short period of time after separation from the aqueous solution (e.g., 1-30 minutes, inclusive), the shape-modified fibers can then be heated to a temperature that is sufficient to rapidly cure the methylolated phenol inside of the reinforcing fibers. For example, the fibers can be heated in an oven for 15-60 minutes, inclusive, at a temperature of 120-200 °C, inclusive, so as to cure the methylolated phenol in the fiber. Upon curing, the dog-bone shape of the reinforcing fibers will be fixed, or at least resistant to further geometric alteration.

Alternatively or additionally, in some aspects, the swelling of the fibers to have the dog-bone shape may occur after the curing of the water blocking agent therein. In some aspects, the exposure of process block 152 can be after the fibers are incorporated with concrete or cement, for example, during the mixing with wet concrete or cement and/or the setting (or drying) of the concrete or cement. The axial ends of the fibers may thus swell *in situ* as the concrete or cement sets to form the dog-bone shape that helps lock the fibers in place therein. In some aspects, the loading of water blocking agent in the lignocellulosic fibers can be tailored to the particular application, for example, such that the water content and drying rate of the concrete or cement matches the water infiltration and corresponding thickness swelling rates for the lignocellulosic fiber. In some aspects, the fiber can non-uniformly swell to reach the desired dog-bone shape once the concrete has set, as opposed to uniform swelling that might occur via prolonged water exposure.

In some aspects, the processing of process block 142 can optionally include altering the surfaces of the lignocellulosic fibers prior to use (e.g., inclusion in the concrete or cement). For example, the surface of the fiber can be treated with mild oxidizing agents to increase the surface energy and bonding potential of the fiber surface. Such oxidizing agents can include, but are not limited to, hydrogen peroxide. Alternatively, the surface of the fiber can be treated with one or more agents that increase the surface porosity of the fiber. Such agents can include, but are not limited to, pulping agents (e.g., sodium sulfite, hydrogen peroxide, etc.).

Alternatively or additionally, in some aspects, the surface of the fiber can be treated with one or more acids, for example, to establish an acidic fiber surface that could offer enhanced bonding to cement. For example, acids suitable for this can include, but are not limited to, dilute aqueous solutions of organic acids (e.g., acetic acid), and inorganic acids (e.g., nitric acid, sulfuric acid, hydrochloric acid, or a combination thereof). In some aspects, the fibers can be washed with water and dried after being treated on the surface with chemicals. Treatments of this sort can result in fibers with unique, outer layers, which can provide improved bonding to cement.

Alternatively or additionally, in some aspects, the processing of process block 142 can optionally include coating the surface of the lignocellulosic fibers prior to use (e.g., including in the concrete or cement). For example, the surface of the fiber can be coated with one or more agents or polymers, such as but not limited to alginates or other anionic polymers, resins, or latexes. In some aspect, the coating with agents or polymers can improve the ability of the fiber to bond to cement mortar. Alternatively or additionally, in some aspects, the processing of process block 142 can optionally include embossing, stamping, patterning, or otherwise treating to modify the topography of the surface. In some aspects, such surface modification can improve the ability of the fiber to bond to cement mortar. Alternatively or additionally, in some aspects, the processing of process block 142 can optionally include thermally modifying the fiber, or at least the surface thereof, with heat treatment.

Although blocks 102-142 of method 100 and blocks 152-158 of method 150 have been described as being performed once, in some aspects, multiple repetitions of a particular process block may be employed before proceeding to the next decision block or process block. In addition, although blocks 102-142 of method 100 and blocks 152-158 of method 150 have been separately illustrated and described, in some aspects, process blocks may be combined and performed together (simultaneously or sequentially). Moreover, although FIGS. 1A-1B illustrate a particular order for blocks 102-142 and blocks 152-158, respectively, aspects of the disclosed subject matter are not limited thereto. Indeed, in certain aspects, the blocks may occur in a different order than illustrated or simultaneously with other blocks. In some aspects, method 100 can include steps or other aspects not specifically illustrated in FIG. 1A, and/or method 150 can include steps or other aspects not specifically illustrated in FIG. 1B. Alternatively or additionally, in some aspects, method 100 may comprise only some of blocks 102-142 of FIG. 1A, and/or method 150 may comprise only some of blocks 152-158 of FIG. 1B.

Modified plant material products prepared in accordance with the present disclosure have density and strength values that are much greater than that of the original starting plant material. Furthermore, the hydration behavior of the modified products is substantially different than that which would be achieved if sections of the plant material were simply compressed in a hot-press in the absence of the treatment with water blocking agent as described herein. Specifically, the disclosed method of preparation results in high-density plant material products with substantially reduced swelling potential and controllable swelling that can yield advantageous fiber shapes for reinforcing concrete or cement.

Without being bound by any particular theory, it is presently believed that when water is absorbed into conventional wood, the water initially absorbs into the cell wall tissue. Specifically, the water absorbs into regions of the cell wall that contain amorphous cellulose and/or hemicellulose. In contrast, relatively little absorption of the water occurs in the lignin-based regions of the wood. Until the cell wall becomes saturated, which is usually at an absorbed water mass of about 28-30% of the dry wood, the water does not fill the cell lumens, although the lumen can hold water if the cell wall is saturated. More than 90% of the swelling in conventional solid wood that occurs when the wood becomes wet is specifically due to swelling of the cell wall. Filling the lumens in the wood with water is typically associated with very little dimensional change in the solid wood.

In some aspects, the methylolated phenol monomers disclosed herein are unique in their ability to absorb into the cell walls of wood in a manner that is similar to that which can be achieved with water molecules. Furthermore, the methylolated phenol monomers have the ability to polymerize at elevated temperatures subsequent to the absorption process. In this process, hemicellulose and amorphous cellulose regions in the wood cell walls, which are normally able to receive water molecules, become occupied with the small methylolated phenol molecules. Upon polymerization, the absorbed methylolated phenol compounds form an intractable, brittle network within the cell wall. This network cannot be removed by extraction and effectively prevents, or at least significantly reduces, future water absorption into this portion of the wood that is responsible for most of the normal swelling that occurs when the wood is exposed to water.

Although many coatings and sealants commercially exist for improving the water-resistance of wood, these coatings and sealants generally operate by creating a layer on the outer surface of the wood. In many cases, these coatings are hydrophobic and effectively reduce the rate at which water absorbs into the treated wood article. However, if the exposure to water occurs over a sufficiently long period of time, then the wood article will fully hydrate and swell. As swelling occurs, the applied coating can sometimes crack and/or detach from the surface of the article. Thus, these technologies operate with a protective mechanism that is fundamentally different than that associated with the hydrophilic monomers, such as methylolated phenol, because the polymer-infiltrated wood fibers do not suffer from cracking and/or detachment concerns to the same extent as externally applied coatings. Nevertheless, waxes, sizing agents, coatings, paints, sealants, and other materials that can be applied to the surface of the treated, infiltrated, and compressed plant material in order to reduce the water absorption rate, swelling rate, and/or general extent of water absorption and swelling, are within the scope of this disclosure. In some examples, the waxes, sizing agents, coatings, paints, and/or sealants can be used in place of the hydrophilic monomers.

The disclosed water blocking agents also have several advantages over penetrating oils (such as tung oil and alkyd resins) and reactive hydrophobic monomers (such as styrene, methacrylate monomers, and isocyanates). In some aspects, the surface tension properties of these penetrating oils and reactive hydrophobic monomers can be different than those of the disclosed hydrophilic monomers as water blocking agent. As a consequence, these penetrating oils and reactive hydrophobic monomers may not be effectively absorbed by the regions of the wood anatomy that are responsible for swelling. Furthermore, while the absorbed oils are hydrophobic and many of them can slow down the water absorption event, said wood articles treated with such oils will eventually fully hydrate and swell if exposed to water for a sustained period of time. Additionally, the very hydrophobic nature of these compounds prevents them from being absorbed by the specific regions of the cell wall that normally absorb the water. Thus, these penetrating oils and reactive hydrophobic monomers may provide a lesser degree of protection than can be achieved by the treatment process disclosed herein.

In some aspects, water-resistance in the wood product (or other plant materials) can be achieved by using a hydrophilic set of small molecules that will spontaneously absorb into amorphous cellulose and hemicellulose regions of the cell wall and that are also capable of thermosetting. Surprisingly, it has been discovered that, while a vastly different approach to that pursued by hydrophobic coatings, and while it might be expected that hydrophilic molecules would increase the tendency of a material to absorb water, the specific affinity of these hydrophilic treatment molecules for the same sites that would ordinarily absorb water, unexpectedly improves water resistance and reduces the propensity of the material to absorb water. Nevertheless, penetrating oils and hydrophobic monomers that can be applied to the surface of the treated, infiltrated, and compressed wood in order to reduce the water absorption rate, swelling rate, and/or general extent of water absorption and swelling, are within the scope of this disclosure. In some examples, the penetrating oils and/or hydrophobic monomers can be used in place of the hydrophilic monomers.

FIG. 4 is a graph showing the swelling thickness over time of untreated natural MettleWood and treated natural MettleWood using the treatment process disclosed herein. Specifically, the experimentally measured swelling of the thickness of densified, lignin-modified wood (MettleWood) fibers versus exposure time was determined for a non-treated specimen; a specimen treated with a solution having a 9% water blocking agent concentration; a specimen treated with a solution having a 26% water blocking agent concentration; and a specimen treated with a solution having a 53% water blocking agent concentration. After each specimen was infiltrated with the solution comprising the blocking agent, the weight uptake was determined. Accordingly, FIG. 4

demonstrates that the swelling time of the densified, lignin-modified wood (MettleWood) fibers can be controlled by treating MettleWood with increasing concentrations of water blocking agents and further adds resistance by having the fibers swell from the axial ends.

FIGS. 5A-5D are photographs of fractured fiber-reinforced concrete blocks, showing the dog-bone shape of densified, lignin-modified wood fibers achieved by the treatment process disclosed herein. The severed concrete blocks show the densified, lignin-modified wood fibers treated with less than 3% water blocking agent exhibiting swelling of the axial end, while the swell of the interior exhibited relatively little or no swelling.

FIG. 6A is a photograph of two dog-bone shaped fibers from a sample of densified, lignin-modified wood fibers treated with less than 3% water blocking agent. The top fiber (labeled "before swell/dry") is a treated fiber with no water exposure. The bottom fiber (labeled "after swell/wet") is a treated fiber submerged in water for 10 minutes. FIG. 6A and FIG. 6B (showing the axial end of the two fibers) demonstrate the swelling of the axial ends of the densified, lignin-modified wood fibers, while the interior exhibited relatively little or no swelling.

Additional Examples of the Disclosed Technology

In view of the above-described implementations of the disclosed subject matter, this application discloses the additional examples in the clauses enumerated below. It should be noted that one feature of a clause in isolation, or more than one feature of the clause taken in combination, and, optionally, in combination with one or more features of one or more further clauses are further examples also falling within the disclosure of this application.

Clause 1. A method comprising:

processing an initial plant material such that native lignin therein is degraded, the processing comprising modifying the native lignin within the initial plant material and/or removing at least a portion of the native lignin from the initial plant material;

forming a water blocking agent on and/or within the processed plant material;

densifying the processed plant material; and

forming the processed plant material into individual lignocellulosic fibers, each having a cross-sectional dimension less than or equal to 5 mm.

Clause 2. The method of any clause or example herein, in particular, Clause 1, further comprising:

mixing the lignocellulosic fibers into wet concrete or cement; and

drying or setting the concrete or cement with the lignocellulosic fibers therein.

Clause 3. The method of any clause or example herein, in particular, Clause 2, wherein:

prior to the mixing, one, some, or all of the lignocellulosic fibers have a substantially rectangular shape in a side view;

after the drying or setting, the one, some, or all of the lignocellulosic fibers have a dog-bone shape in a side view, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions; and

the dog-bone shape is formed *in situ* by swelling of the axial end portions via water infiltration from the wet concrete or cement during the mixing and/or drying or setting.

Clause 4. The method of any clause or example herein, in particular, Clause 2, further comprising, after the forming individual lignocellulosic fibers and prior to the mixing, modifying a shape of one, some, or all of the lignocellulosic fibers to have a dog-bone shape in a side view, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

Clause 5. The method of any clause or example herein, in particular, Clause 4, wherein:

prior to the modifying to have the dog-bone shape, the one, some, or all of the lignocellulosic fibers have a substantially rectangular shape in a side view; and

the modifying to have the dog-bone shape comprises exposing the one, some, or all of the lignocellulosic fibers to an aqueous environment, such that the axial end portions swell via water infiltration.

Clause 6. The method of any clause or example herein, in particular, any one of Clauses 3-5, wherein a loading of the water blocking agent within the processed plant material and a duration of exposure to water are selected such that a swelling of the intermediate portion is less than the axial end portions, thereby forming the dog-bone shape.

Clause 7. The method of any clause or example herein, in particular, any one of Clauses 4-5, further comprising, after the modifying, subjecting the one, some, or all of the lignocellulosic fibers having the dog-bone shape to heating at an elevated temperature, such that the dog-bone shape thereof becomes fixed.

Clause 8. The method of any clause or example herein, in particular, Clause 7, wherein the heating at the elevated temperature cures the water blocking agent and/or cross-links with components in the respective lignocellulosic fiber.

Clause 9. The method of any clause or example herein, in particular, any one of Clauses 7-8, wherein the elevated temperature is in a range of 50-250 °C, inclusive.

Clause 10. The method of any clause or example herein, in particular, any one of Clauses 7-9, wherein the subjecting to heating at the elevated temperature is for a time in a range of 1-200 minutes, inclusive.

Clause 11. The method of any clause or example herein, in particular, any one of Clauses 1-2, wherein the forming into lignocellulosic fibers comprises mechanically shaping one, some, or all of the lignocellulosic fibers to have a non-rectangular shape in a side view.

Clause 12. The method of any clause or example herein, in particular, Clause 11, wherein the non-rectangular shape is a dog-bone shape, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

Clause 13. The method of any clause or example herein, in particular, any one of Clauses 3-12, wherein, after the drying or setting, the non-rectangular or dog-bone shape locks the respective lignocellulosic fiber in place within the dried/set concrete or cement.

Clause 14. The method of any clause or example herein, in particular, any one of Clauses 1-13, wherein the forming a water blocking agent comprises:

infiltrating the processed plant material with a solution comprising the water blocking agent and/or precursors for the water blocking agent, such that the water blocking agent and/or water blocking agent precursors are absorbed within amorphous cellulose and hemicellulose regions of one or more cell walls of the processed plant material; and

crosslinking the amorphous cellulose and/or hemicellulose regions with the water blocking agent after infiltrating the processed plant material with the solution.

Clause 15. The method of any clause or example herein, in particular, Clause 14, wherein a level of swelling of the lignocellulosic fibers with the water blocking agent therein along a respective thickness direction of the lignocellulosic fibers is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the lignocellulosic fibers.

Clause 16. The method of any clause or example herein, in particular, any one of Clauses 14-15, wherein:

the water blocking agent precursors comprise a nucleophile and an electrophile, and the water blocking agent comprises a reaction product of the nucleophile and the electrophile; and each of the water blocking agent and the water blocking agent precursors has a molecular weight less than or equal to 500 g/mole when infiltrating the processed plant material with the solution.

Clause 17. The method of any clause or example herein, in particular, Clause 16, wherein:

the nucleophile comprises an aromatic nucleophile; and

the electrophile comprises (i) an aldehyde, an oxirane, an oxazolidine, or a bisoxazolidine; (ii) both the aldehyde and the oxazolidine; or (iii) both the aldehyde and the bisoxazolidine.

Clause 18. The method of any clause or example herein, in particular, Clause 17, wherein:

(i) the aromatic nucleophile comprises phenol or cresol;

(ii) the electrophile is soluble in water;

(iii) the aldehyde comprises formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, or glutaraldehyde; or

(iv) any combination of two or more of (i), (ii), and (iii).

Clause 19. The method of any clause or example herein, in particular, any one of Clauses 16-18, wherein the nucleophile is phenol, the electrophile is formaldehyde, the water blocking agent precursors are monomers and/or oligomers of methylolated phenol, and each oligomer, if present, has a molecular weight of 500 g/mole or less.

Clause 20. The method of any clause or example herein, in particular, Clause 19, wherein a molar ratio of formaldehyde to phenol for the water blocking agent precursors is in a range of 1:1 to 3:1, inclusive.

Clause 21. The method of any clause or example herein, in particular, any one of Clauses 14-20, wherein:

(i) the solution comprising the water blocking agent and/or water blocking agent precursors is an aqueous solution;

(ii) the solution has a viscosity in a range of 1-40 cPs, inclusive, at 20 °C;

(iii) the water blocking agent and/or the water blocking agent precursors are present in amounts ranging from 1-70%, inclusive, of a mass of the solution; or

(iv) any combination of two or more of (i), (ii), and (iii).

Clause 22. The method of any clause or example herein, in particular, any one of Clauses 1-13, wherein the water blocking agent comprises a hydrophilic reactive monomer.

Clause 23. The method of any clause or example herein, in particular, Clause 22, wherein the hydrophilic reactive monomer comprises methylolated phenol, methylolated cresol, a methylolated substituted phenol, or any combination of the foregoing.

Clause 24. The method of any clause or example herein, in particular, any one of Clauses 1-23, wherein the water blocking agent comprises a hydrophobic reactive monomer, a wax, a sizing agent, a drying oil, a topical sealant, or a coating configured to reduce water absorption.

Clause 25. The method of any clause or example herein, in particular, any one of Clauses 1-24, wherein the processing such that native lignin is degraded comprises:

infiltrating the initial plant material with a loading solution; and

subjecting the initial plant material, with the loading solution therein, to a first temperature and a first pressure so as to modify the native lignin and provide a modified lignin,

wherein the first temperature is in a range of 20-200 °C, inclusive, and the first pressure is in a range of 1-8 bar, inclusive.

Clause 26. The method of any clause or example herein, in particular, Clause 25, wherein the loading solution comprises sodium hydroxide, sodium sulfite, an oxidizing agent, or any combination of the foregoing.

Clause 27. The method of any clause or example herein, in particular, Clause 26, wherein the oxidizing agent comprises ozone, oxygen, hydrogen peroxide, or an organic peroxide.

Clause 28. The method of any clause or example herein, in particular, any one of Clauses 25-27, wherein the loading solution comprises water.

Clause 29. The method of any clause or example herein, in particular, any one of Clauses 25-28, wherein the loading solution comprises one or more non-volatile amines.

Clause 30. The method of any clause or example herein, in particular, Clause 29, wherein the non-volatile amine is ethanolamine, diethanolamine, triethanolamine, hydroxylamine, triethylamine, hexylamine, butylamine, dibutylamine, methanolamine, dimethanolamine, trimethanolamine, propanolamine, dipropanolamine, tripropanolamine, 2-amino-2-methyl-1-propanol, or valinol.

Clause 31. The method of any clause or example herein, in particular, any one of Clauses 25-30, wherein:

a water content of the initial plant material is in a range of 1-20 wt%, inclusive prior to infiltrating the initial plant material with the loading solution; and the water content of the initial plant material is in a range of 20-100 wt%, inclusive after infiltrating the initial plant material with the loading solution and prior to subjecting the initial plant material, with the loading solution therein, to the first temperature and pressure.

Clause 32. The method of any clause or example herein, in particular, any one of Clauses 25-31, wherein a molecular weight of the modified lignin is reduced as compared to that of native lignin in the initial plant material, and the modified lignin is insoluble in water at room temperature.

Clause 33. The method of any clause or example herein, in particular, any one of Clauses 1-23, wherein the processing such that native lignin is degraded comprises:

subjecting the initial plant material to a chemical delignification treatment so as to remove a portion, but not all, of the native lignin from the initial plant material.

Clause 34. The method of any clause or example herein, in particular, Clause 33, wherein:

subjecting the initial plant material to the chemical delignification treatment comprises partial or full immersion of the initial plant material in one or more chemical solutions at a temperature of at least 100 °C, and

the one or more chemical solutions comprise an alkaline solution.

Clause 35. The method of any clause or example herein, in particular, any one of Clauses 33-34, wherein a lignin content of the processed plant material after degrading the native lignin of the initial plant material is between 5% and 95%, inclusive, of a lignin content of the initial plant material.

Clause 36. The method of any clause or example herein, in particular, any one of Clauses 1-35, further comprising drying the processed plant material to have a water content of 1-20 wt%, inclusive, after the processing and prior to the forming the water blocking agent.

Clause 37. The method of any clause or example herein, in particular, any one of Clauses 1-36, wherein the densifying comprises compressing the processed plant material with the water blocking agent or precursors of the water blocking agent therein, such that the processed plant material has a first density of at least 900 kg/m^3.

Clause 38. The method of any clause or example herein, in particular, Clause 37, wherein the first density is in a range of 900-1200 kg/m^3, inclusive.

Clause 39. The method of any clause or example herein, in particular, any one of Clauses 37-38, wherein the compressing is performed at a temperature in a range of 20-150 °C, inclusive, and a pressure in a range of 3-8 MPa, inclusive.

Clause 40. The method of any clause or example herein, in particular, any one of Clauses 37-39, wherein the compressing is performed at a temperature in a range of 20-60 °C.

Clause 41. The method of any clause or example herein, in particular, any one of Clauses 37-40, further comprising:

drying the processed plant material to a moisture content in a range of 15-25 wt%, inclusive, prior to compressing the processed plant material; and

drying the processed plant material to have a water content of 1-10 wt%, inclusive, after compressing the processed plant material.

Clause 42. The method of any clause or example herein, in particular, Clause 41, further comprising further compressing the processed plant material after the drying the to have a water content of 1-10 wt%, such that the processed plant material has a second density of at least 1200 kg/m^3.

Clause 43. The method of any clause or example herein, in particular, Clause 42, wherein the second density is in a range of 1200-1450 kg/m^3, inclusive.

Clause 44. The method of any clause or example herein, in particular, any one of Clauses 42-43, wherein the further compressing the first plant material is performed at a temperature in a range of 20-200 °C, inclusive, and a pressure in a range of 3-10 MPa, inclusive.

Clause 45. The method of any clause or example herein, in particular, any one of Clauses 1-44, wherein the water blocking agent is formed by curing and/or crosslinking after and/or during the densifying.

Clause 46. The method of any clause or example herein, in particular, any one of Clauses 1-45, wherein the initial plant material is wood.

Clause 47. The method of any clause or example herein, in particular, any one of Clauses 1-46, wherein, for one, some, or each of the lignocellulosic fibers:

the cross-sectional dimension is in a range of 0.5-5 mm, inclusive;
a length thereof is in a range of 10-150 mm, inclusive;
a modulus in a longitudinal axis thereof is in a range of 25-50 GPa, inclusive;
a thermal expansion coefficient thereof is less than or equal to 2×10^{-5} m/(m·°C); or
any combination of the above.

Clause 48. The method of any clause or example herein, in particular, any one of Clauses 1-47, wherein the forming into individual lignocellulosic fibers comprises cutting the processing plant material.

Clause 49. The method of any clause or example herein, in particular, any one of Clauses 1-48, wherein the forming the water blocking agent is performed after the densifying.

Clause 50. The method of any clause or example herein, in particular, any one of Clauses 1-49, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with a pulping agent.

Clause 51. The method of any clause or example herein, in particular, Clause 50, wherein the pulping agent comprises sodium sulfite.

Clause 52. The method of any clause or example herein, in particular, any one of Clauses 1-51, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an oxidizing agent.

Clause 53. The method of any clause or example herein, in particular, Clause 52, wherein the oxidizing agent comprises hydrogen peroxide, oxygen, ozone, or any combination of the foregoing.

Clause 54. The method of any clause or example herein, in particular, any one of Clauses 1-53, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an organic acidic agent.

Clause 55. The method of any clause or example herein, in particular, Clause 54, wherein the organic acidic agent comprises acetic acid, citric acid, tartaric acid, or any combination of the foregoing.

Clause 56. The method of any clause or example herein, in particular, any one of Clauses 1-55, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an inorganic acidic agent.

Clause 57. The method of any clause or example herein, in particular, Clause 56, wherein the inorganic acidic agent comprises nitric acid, sulfuric acid, hydrochloric acid, or any combination of the foregoing.

Clause 58. The method of any clause or example herein, in particular, any one of Clauses 1-57, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treating with a coating.

Clause 59. The method of any clause or example herein, in particular, Clause 58, wherein the coating comprises an anionic polymer, a resin, a latex, or any combination of the foregoing.

Clause 60. The method of any clause or example herein, in particular, any one of Clauses 1-59, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers so as to change a topography of said surfaces.

Clause 61. The method of any clause or example herein, in particular, Clause 60, wherein the modifying to change the topography comprises embossing, etching, stamping or any combination of the foregoing.

Clause 62. The method of any clause or example herein, in particular, any one of Clauses 1-61, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by subjecting to a heat treatment.

Clause 63. A structure formed by the method of any clause or example herein, in particular, any one of Clauses 1-62.

Clause 64. A structure comprising:

a plurality of lignocellulosic fibers, each having a cross-sectional dimension less than or equal to 5 mm; and

a water blocking agent on and/or within the plurality of lignocellulosic fibers.

Clause 65. The structure of any clause or example herein, in particular, Clause 64, further comprising concrete or cement, wherein the plurality of lignocellulosic fibers are dispersed within the concrete or the cement.

Clause 66. The structure of any clause or example herein, in particular, any one of Clauses 63-65, wherein one, some, or each of the lignocellulosic fibers has a non-rectangular shape in a side view.

Clause 67. The structure of any clause or example herein, in particular, Clause 66, wherein the non-rectangular shape is a dog-bone shape, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

Clause 68. The structure of any clause or example herein, in particular, any one of Clauses 66-67, wherein the non-rectangular shape locks the respective lignocellulosic fiber in place within the concrete or the cement.

Clause 69. The structure of any clause or example herein, in particular, any one of Clauses 63-68, wherein each lignocellulosic fiber is formed from plant material having cell walls comprising an amorphous cellulose region and a hemicellulose region, and the water blocking agent crosslinks the amorphous cellulose region and the hemicellulose region of the cell walls of the plant material.

Clause 70. The structure of any clause or example herein, in particular, Clause 69, wherein a level of swelling of the lignocellulosic fibers, with the water blocking agent therein along a respective thickness direction of the lignocellulosic fibers is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the lignocellulosic fibers.

Clause 71. The structure of any clause or example herein, in particular, any one of Clauses 69-70, wherein the water blocking agent comprises a reaction product of a nucleophile and an electrophile, and each of the nucleophile, the electrophile, and the water blocking agent has a molecular weight less than or equal to 500 g/mole prior to the crosslinking.

Clause 72. The structure of any clause or example herein, in particular, Clause 71, wherein:

the nucleophile comprises an aromatic nucleophile; and

the electrophile comprises: (i) an aldehyde, an oxirane, an oxazolidine, or a bisoxazolidine; (ii) both the aldehyde and the oxazolidine; or (iii) both the aldehyde and the bisoxazolidine.

Clause 73. The structure of any clause or example herein, in particular, any one of Clauses 63-72, wherein the water blocking agent comprises a hydrophilic reactive monomer.

Clause 74. The structure of any clause or example herein, in particular, Clause 73, wherein the hydrophilic reactive monomer comprises methylolated phenol, methylolated cresol, a methylolated substituted phenol, or any combination of the foregoing.

Clause 75. The structure of any clause or example herein, in particular, any one of Clauses 63-74, wherein the water blocking agent comprises a hydrophobic reactive monomer, a wax, a sizing agent, a drying oil, a topical sealant, or a coating configured to reduce water absorption.

Clause 76. The structure of any clause or example herein, in particular, any one of Clauses 63-75, wherein at least a portion of a lignin in the lignocellulosic fibers is modified as compared to a lignin of a native plant material from which the lignocellulosic fibers are formed.

Clause 77. The structure of any clause or example herein, in particular, Clause 76, wherein a molecular weight of the modified lignin is reduced as compared to that of the lignin in the native plant material, and the modified lignin is insoluble in water at room temperature.

Clause 78. The structure of any clause or example herein, in particular, any one of Clauses 63-77, wherein a lignin content of the lignocellulosic fibers is less than that of a native plant material from which the lignocellulosic fibers are formed.

Clause 79. The structure of any clause or example herein, in particular, any one of Clauses 63-78, wherein the lignocellulosic fibers have densities greater than or equal to 900 kg/m^3.

Clause 80. The structure of any clause or example herein, in particular, any one of Clauses 63-79, wherein the lignocellulosic fibers have densities greater than or equal to 1200 kg/m^3.

Clause 81. The structure of any clause or example herein, in particular, any one of Clauses 63-80, wherein the lignocellulosic fibers have densities in a range of 1200-1450 kg/m^3, inclusive.

Clause 82. The structure of any clause or example herein, in particular, any one of Clauses 63-81, wherein:

each of the lignocellulosic fibers is formed from plant material having native lumina defined by one or more plant cell walls; and

each of the lignocellulosic fibers is a densified piece with the native lumina therein collapsed.

Clause 83. The structure of any clause or example herein, in particular, any one of Clauses 63-82, wherein the plant material is wood.

Clause 84. The structure of any clause or example herein, in particular, any one of Clauses 63-83, wherein, for one, some, or each of the lignocellulosic fibers:

the cross-sectional dimension is in a range of 0.5-5 mm, inclusive;
a length thereof is in a range of 10-150 mm, inclusive;
a modulus in a longitudinal axis thereof is in a range of 25-50 GPa, inclusive;
a thermal expansion coefficient thereof is less than or equal to 2×10^{-5} m/(m·°C); or
any combination of the above.

Clause 85. The structure of any clause or example herein, in particular, any one of Clauses 63-84, wherein surfaces of one, some, or each of the lignocellulosic fibers has been modified by treatment with a pulping agent, an oxidizing agent, an organic acidic agent, or an inorganic acidic agent.

Clause 86. The structure of any clause or example herein, in particular, any one of Clauses 63-85, wherein surfaces of one, some, or each of the lignocellulosic fibers has been modified by treatment with a coating.

Conclusion

Any of the features illustrated or described herein, for example, with respect to FIGS. 1-5B and Clauses 1-86, can be combined with any other feature illustrated or described herein, for example, with respect to FIGS. 1-5B and Clauses 1-86 to provide materials, systems, devices, structures, methods, and aspects not otherwise illustrated or specifically described herein. All features described herein are independent of one another and, except where structurally impossible, can be used in combination with any other feature described herein. In view of the many possible aspects to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated aspects are only examples and should not be taken as limiting the scope of the disclosed technology. Rather, the scope is defined by the following claims. We therefore claim all that comes within the scope and spirit of these claims.

CLAIMS

1. A method, comprising:

processing an initial plant material such that native lignin therein is degraded, the processing comprising modifying the native lignin within the initial plant material and/or removing at least a portion of the native lignin from the initial plant material;

forming a water blocking agent on and/or within the processed plant material;

densifying the processed plant material; and

forming the processed plant material into individual lignocellulosic fibers, each having a cross-sectional dimension less than or equal to 5 mm.

2. The method of claim 1, further comprising:

mixing the lignocellulosic fibers into wet concrete or cement; and

drying or setting the concrete or cement with the lignocellulosic fibers therein.

3. The method of claim 2, wherein:

prior to the mixing, one, some, or all of the lignocellulosic fibers have a substantially rectangular shape in a side view;

after the drying or setting, the one, some, or all of the lignocellulosic fibers have a dog-bone shape in a side view, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions; and

the dog-bone shape is formed *in situ* by swelling of the axial end portions via water infiltration from the wet concrete or cement during the mixing and/or drying or setting.

4. The method of claim 2, further comprising, after the forming individual lignocellulosic fibers and prior to the mixing, modifying a shape of one, some, or all of the lignocellulosic fibers to have a dog-bone shape in a side view, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

5. The method of claim 4, wherein:

prior to the modifying to have the dog-bone shape, the one, some, or all of the lignocellulosic fibers have a substantially rectangular shape in a side view; and the modifying to have the dog-bone shape comprises exposing the one, some, or all of the lignocellulosic fibers to an aqueous environment, such that the axial end portions swell via water infiltration.

6. The method of any one of claims 3-5, wherein a loading of the water blocking agent within the processed plant material and a duration of exposure to water are selected such that a swelling of the intermediate portion is less than the axial end portions, thereby forming the dog-bone shape.

7. The method of any one of claims 4-5, further comprising, after the modifying, subjecting the one, some, or all of the lignocellulosic fibers having the dog-bone shape to heating at an elevated temperature, such that the dog-bone shape thereof becomes fixed.

8. The method of claim 7, wherein the heating at the elevated temperature cures the water blocking agent and/or cross-links with components in the respective lignocellulosic fiber.

9. The method of claim 7, wherein the elevated temperature is in a range of 50-250 °C, inclusive.

10. The method of claim 7, wherein the subjecting to heating at the elevated temperature is for a time in a range of 1-200 minutes, inclusive.

11. The method of claim 2, wherein the forming into lignocellulosic fibers comprises mechanically shaping one, some, or all of the lignocellulosic fibers to have a non-rectangular shape in a side view.

12. The method of claim 11, wherein the non-rectangular shape is a dog-bone shape, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

13. The method of any one of claims 3-12, wherein, after the drying or setting, the non-rectangular or dog-bone shape locks the respective lignocellulosic fiber in place within the set concrete or cement.

14. The method of claim 1, wherein the forming a water blocking agent comprises:

infiltrating the processed plant material with a solution comprising the water blocking agent and/or precursors for the water blocking agent, such that the water blocking agent and/or water blocking agent precursors are absorbed within amorphous cellulose and hemicellulose regions of one or more cell walls of the processed plant material; and

crosslinking the amorphous cellulose and/or hemicellulose regions with the water blocking agent after infiltrating the processed plant material with the solution.

15. The method of claim 14, wherein a level of swelling of the lignocellulosic fibers with the water blocking agent therein along a respective thickness direction of the lignocellulosic fibers is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the lignocellulosic fibers.

16. The method of claim 14, wherein:

the water blocking agent precursors comprise a nucleophile and an electrophile, and the water blocking agent comprises a reaction product of the nucleophile and the electrophile; and

each of the water blocking agent and the water blocking agent precursors has a molecular weight less than or equal to 500 g/mole when infiltrating the processed plant material with the solution.

17. The method of claim 16, wherein:

the nucleophile comprises an aromatic nucleophile; and

the electrophile comprises (i) an aldehyde, an oxirane, an oxazolidine, or a bisoxazolidine; (ii) both the aldehyde and the oxazolidine; or (iii) both the aldehyde and the bisoxazolidine.

18. The method of claim 17, wherein:

(i) the aromatic nucleophile comprises phenol or cresol;

(ii) the electrophile is soluble in water;

(iii) the aldehyde comprises formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, or glutaraldehyde; or

(iv) any combination of two or more of (i), (ii), and (iii).

19. The method of claim 16, wherein the nucleophile is phenol, the electrophile is formaldehyde, the water blocking agent precursors are monomers and/or oligomers of methylolated phenol, and each oligomer, if present, has a molecular weight of 500 g/mole or less.

20. The method of claim 19, wherein a molar ratio of formaldehyde to phenol for the water blocking agent precursors is in a range of 1:1 to 3:1, inclusive.

21. The method of claim 14, wherein:

(i) the solution comprising the water blocking agent and/or water blocking agent precursors is an aqueous solution;

(ii) the solution has a viscosity in a range of 1-40 cPs, inclusive, at 20 °C;

(iii) the water blocking agent and/or the water blocking agent precursors are present in amounts ranging from 1-70%, inclusive, of a mass of the solution; or

(iv) any combination of two or more of (i), (ii), and (iii).

22. The method of claim 1, wherein the water blocking agent comprises a hydrophilic reactive monomer.

23. The method of claim 22, wherein the hydrophilic reactive monomer comprises methylolated phenol, methylolated cresol, a methylolated substituted phenol, or any combination of the foregoing.

24. The method of claim 1, wherein the water blocking agent comprises a hydrophobic reactive monomer, a wax, a sizing agent, a drying oil, a topical sealant, or a coating configured to reduce water absorption.

25. The method of claim 1, wherein the processing such that native lignin is degraded comprises:

infiltrating the initial plant material with a loading solution; and

subjecting the initial plant material, with the loading solution therein, to a first temperature and a first pressure so as to modify the native lignin and provide a modified lignin,

wherein the first temperature is in a range of 20-200 °C, inclusive, and the first pressure is in a range of 1-8 bar, inclusive.

26. The method of claim 25, wherein the loading solution comprises sodium hydroxide, sodium sulfite, an oxidizing agent, or any combination of the foregoing.

27. The method of claim 26, wherein the oxidizing agent comprises ozone, oxygen, hydrogen peroxide, or an organic peroxide.

28. The method of claim 25, wherein the loading solution comprises water.

29. The method of claim 25, wherein the loading solution comprises one or more non-volatile amines.

30. The method of claim 29, wherein the non-volatile amine is ethanolamine, diethanolamine, triethanolamine, hydroxylamine, triethylamine, hexylamine, butylamine, dibutylamine, methanolamine, dimethanolamine, trimethanolamine, propanolamine, dipropanolamine, tripropanolamine, 2-amino-2-methyl-1-propanol, or valinol.

31. The method of claim 25, wherein:

a water content of the initial plant material is in a range of 1-20 wt%, inclusive prior to infiltrating the initial plant material with the loading solution; and

the water content of the initial plant material is in a range of 20-100 wt%, inclusive after infiltrating the initial plant material with the loading solution and prior to subjecting the initial plant material, with the loading solution therein, to the first temperature and pressure.

32. The method of claim 25, wherein a molecular weight of the modified lignin is reduced as compared to that of native lignin in the initial plant material, and the modified lignin is insoluble in water at room temperature.

33. The method of claim 1, wherein the processing such that native lignin is degraded comprises:

subjecting the initial plant material to a chemical delignification treatment so as to remove a portion, but not all, of the native lignin from the initial plant material.

34. The method of claim 33, wherein:

subjecting the initial plant material to the chemical delignification treatment comprises partial or full immersion of the initial plant material in one or more chemical solutions at a temperature of at least 100 °C, and

the one or more chemical solutions comprise an alkaline solution.

35. The method of claim 33, wherein a lignin content of the processed plant material after degrading the native lignin of the initial plant material is between 5% and 95%, inclusive, of a lignin content of the initial plant material.

36. The method of claim 1, further comprising drying the processed plant material to have a water content of 1-20 wt%, inclusive, after the processing and prior to the forming the water blocking agent.

37. The method of claim 1, wherein the densifying comprises:

compressing the processed plant material with the water blocking agent or precursors of the water blocking agent therein, such that the processed plant material has a first density of at least 900 kg/m^3.

38. The method of claim 37, wherein the first density is in a range of 900-1200 kg/m^3, inclusive.

39. The method of claim 37, wherein the compressing is performed at a temperature in a range of 20-150 °C, inclusive, and a pressure in a range of 3-8 MPa, inclusive.

40. The method of claim 39, wherein the compressing is performed at a temperature in a range of 20-60 °C.

41. The method of claim 37, further comprising:

drying the processed plant material to a moisture content in a range of 15-25 wt%, inclusive, prior to compressing the processed plant material; and

drying the processed plant material to have a water content of 1-10 wt%, inclusive, after compressing the processed plant material.

42. The method of claim 41, further comprising further compressing the processed plant material after the drying the to have a water content of 1-10 wt%, such that the processed plant material has a second density of at least 1200 kg/m^3.

43. The method of claim 42, wherein the second density is in a range of 1200-1450 kg/m^3, inclusive.

44. The method of claim 42, wherein the further compressing the first plant material is performed at a temperature in a range of 20-200 °C, inclusive, and a pressure in a range of 3-10 MPa, inclusive.

45. The method of claim 1, wherein the water blocking agent is formed by curing and/or crosslinking after and/or during the densifying.

46. The method of claim 1, wherein the initial plant material is wood.

47. The method of claim 1, wherein, for one, some, or each of the lignocellulosic fibers:
the cross-sectional dimension is in a range of 0.5-5 mm, inclusive;
a length thereof is in a range of 10-150 mm, inclusive;
a modulus in a longitudinal axis thereof is in a range of 25-50 GPa, inclusive;
a thermal expansion coefficient thereof is less than or equal to 2×10^{-5} m/(m·°C); or
any combination of the above.

48. The method of claim 1, wherein the forming into individual lignocellulosic fibers comprises cutting the processing plant material.

49. The method of claim 1, wherein the forming the water blocking agent is performed after the densifying.

50. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with a pulping agent.

51. The method of claim 50, wherein the pulping agent comprises sodium sulfite.

52. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an oxidizing agent.

53. The method of claim 52, wherein the oxidizing agent comprises hydrogen peroxide, oxygen, ozone, or any combination of the foregoing.

54. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an organic acidic agent.

55. The method of claim 54, wherein the organic acidic agent comprises acetic acid, citric acid, tartaric acid, or any combination of the foregoing.

56. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treatment with an inorganic acidic agent.

57. The method of claim 56, wherein the inorganic acidic agent comprises nitric acid, sulfuric acid, hydrochloric acid, or any combination of the foregoing.

58. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by treating with a coating.

59. The method of claim 58, wherein the coating comprises an anionic polymer, a resin, a latex, or any combination of the foregoing.

60. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers so as to change a topography of said surfaces.

61. The method of claim 60, wherein the modifying to change the topography comprises embossing, etching, stamping or any combination of the foregoing.

62. The method of claim 1, further comprising modifying surfaces of one, some, or each of the lignocellulosic fibers by subjecting to a heat treatment.

63. A structure formed by the method of any one of claims 1-62.

64. A structure comprising:

a plurality of lignocellulosic fibers, each having a cross-sectional dimension less than or equal to 5 mm; and

a water blocking agent on and/or within the plurality of lignocellulosic fibers.

65. The structure of claim 64, further comprising concrete or cement, wherein the plurality of lignocellulosic fibers are dispersed within the concrete or the cement.

66. The structure of any one of claims 64-65, wherein one, some, or each of the lignocellulosic fibers has a non-rectangular shape in a side view.

67. The structure of claim 66, wherein the non-rectangular shape is a dog-bone shape, with thicknesses of axial end portions of the dog-bone shape being greater than a thickness of an intermediate portion of the dog-bone shape between the axial end portions.

68. The structure of claim 66, wherein the non-rectangular shape locks the respective lignocellulosic fiber in place within the concrete or the cement.

69. The structure of any one of claims 64-65, wherein each lignocellulosic fiber is formed from plant material having cell walls comprising an amorphous cellulose region and a hemicellulose region, and the water blocking agent crosslinks the amorphous cellulose region and the hemicellulose region of the cell walls of the plant material.

70. The structure of claim 69, wherein a level of swelling of the lignocellulosic fibers, with the water blocking agent therein along a respective thickness direction of the lignocellulosic fibers is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the lignocellulosic fibers.

71. The structure of claim 69, wherein the water blocking agent comprises a reaction product of a nucleophile and an electrophile, and each of the nucleophile, the electrophile, and the water blocking agent has a molecular weight less than or equal to 500 g/mole prior to the crosslinking.

72. The structure of claim 71, wherein:

the nucleophile comprises an aromatic nucleophile; and

the electrophile comprises: (i) an aldehyde, an oxirane, an oxazolidine, or a bisoxazolidine; (ii) both the aldehyde and the oxazolidine; or (iii) both the aldehyde and the bisoxazolidine.

73. The structure of any one of claims 64-65, wherein the water blocking agent comprises a hydrophilic reactive monomer.

74. The structure of claim 73, wherein the hydrophilic reactive monomer comprises methylolated phenol, methylolated cresol, a methylolated substituted phenol, or any combination of the foregoing.

75. The structure of any one of claims 64-65, wherein the water blocking agent comprises a hydrophobic reactive monomer, a wax, a sizing agent, a drying oil, a topical sealant, or a coating configured to reduce water absorption.

76. The structure of any one of claims 64-65, wherein at least a portion of a lignin in the lignocellulosic fibers is modified as compared to a lignin of a native plant material from which the lignocellulosic fibers are formed.

77. The structure of claim 76, wherein a molecular weight of the modified lignin is reduced as compared to that of the lignin in the native plant material, and the modified lignin is insoluble in water at room temperature.

78. The structure of any one of claims 64-65, wherein a lignin content of the lignocellulosic fibers is less than that of a native plant material from which the lignocellulosic fibers are formed.

79. The structure of any one of claims 64-65, wherein the lignocellulosic fibers have densities greater than or equal to 900 kg/m^3.

80. The structure of any one of claims 64-65, wherein the lignocellulosic fibers have densities greater than or equal to 1200 kg/m^3.

81. The structure of any one of claims 64-65, wherein the lignocellulosic fibers have densities in a range of 1200-1450 kg/m^3, inclusive.

82. The structure of any one of claims 64-65, wherein:

each of the lignocellulosic fibers is formed from plant material having native lumina defined by one or more plant cell walls; and

each of the lignocellulosic fibers is a densified piece with the native lumina therein collapsed.

83. The structure of claim 82, wherein the plant material is wood.

84. The structure of any one of claims 64-65, wherein, for one, some, or each of the lignocellulosic fibers:

the cross-sectional dimension is in a range of 0.5-5 mm, inclusive;

a length thereof is in a range of 10-150 mm, inclusive;

a modulus in a longitudinal axis thereof is in a range of 25-50 GPa, inclusive;

a thermal expansion coefficient thereof is less than or equal to 2×10^{-5} m/(m·°C); or

any combination of the above.

85. The structure of any one of claims 64-65, wherein surfaces of one, some, or each of the lignocellulosic fibers has been modified by treatment with a pulping agent, an oxidizing agent, an organic acidic agent, or an inorganic acidic agent.

86. The structure of any one of claims 64-65, wherein surfaces of one, some, or each of the lignocellulosic fibers has been modified by treatment with a coating.

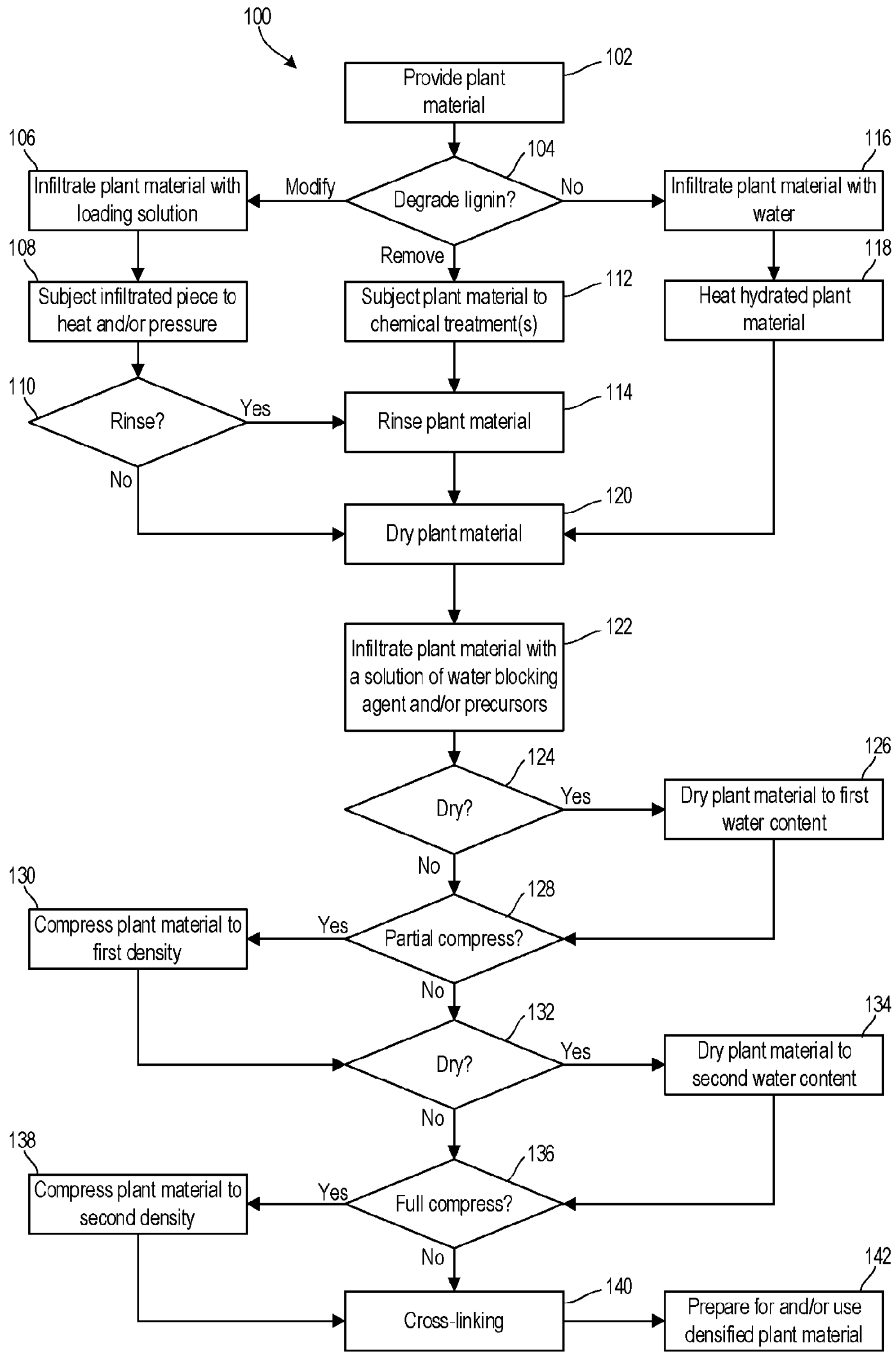
100
Provide plant material
102
Degrade lignin?
104
Modify
No
Remove
106
Infiltrate plant material with loading solution
116
Infiltrate plant material with water
108
Subject infiltrated piece to heat and/or pressure
112
Subject plant material to chemical treatment(s)
118
Heat hydrated plant material
110
Rinse?
Yes
No
114
Rinse plant material
120
Dry plant material
122
Infiltrate plant material with a solution of water blocking agent and/or precursors
124
Dry?
Yes
No
126
Dry plant material to first water content
128
Partial compress?
Yes
No
130
Compress plant material to first density
132
Dry?
Yes
No
134
Dry plant material to second water content
136
Full compress?
Yes
No
138
Compress plant material to second density
140
Cross-linking
142
Prepare for and/or use densified plant material

FIG. 1A

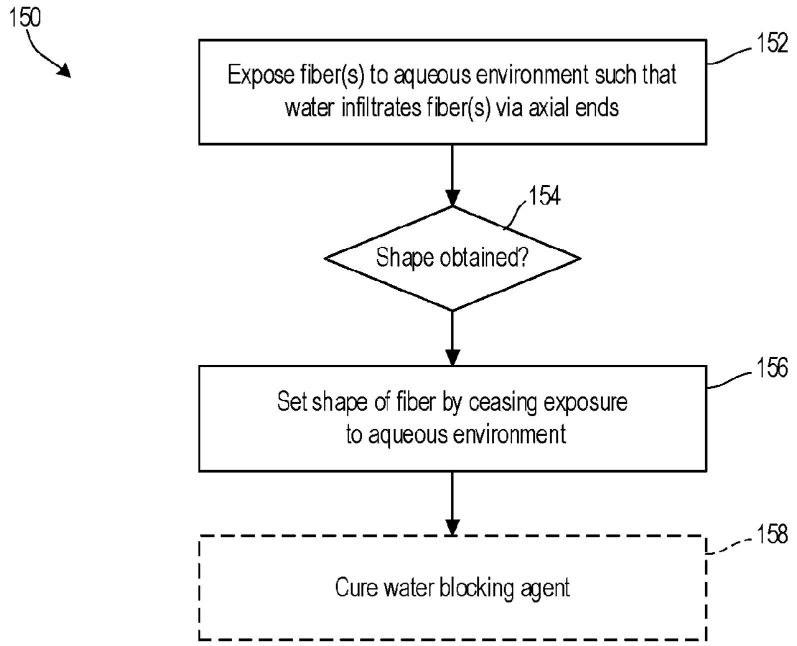
150
Expose fiber(s) to aqueous environment such that water infiltrates fiber(s) via axial ends
152
154
Shape obtained?
Set shape of fiber by ceasing exposure to aqueous environment
156
Cure water blocking agent
158

FIG. 1B

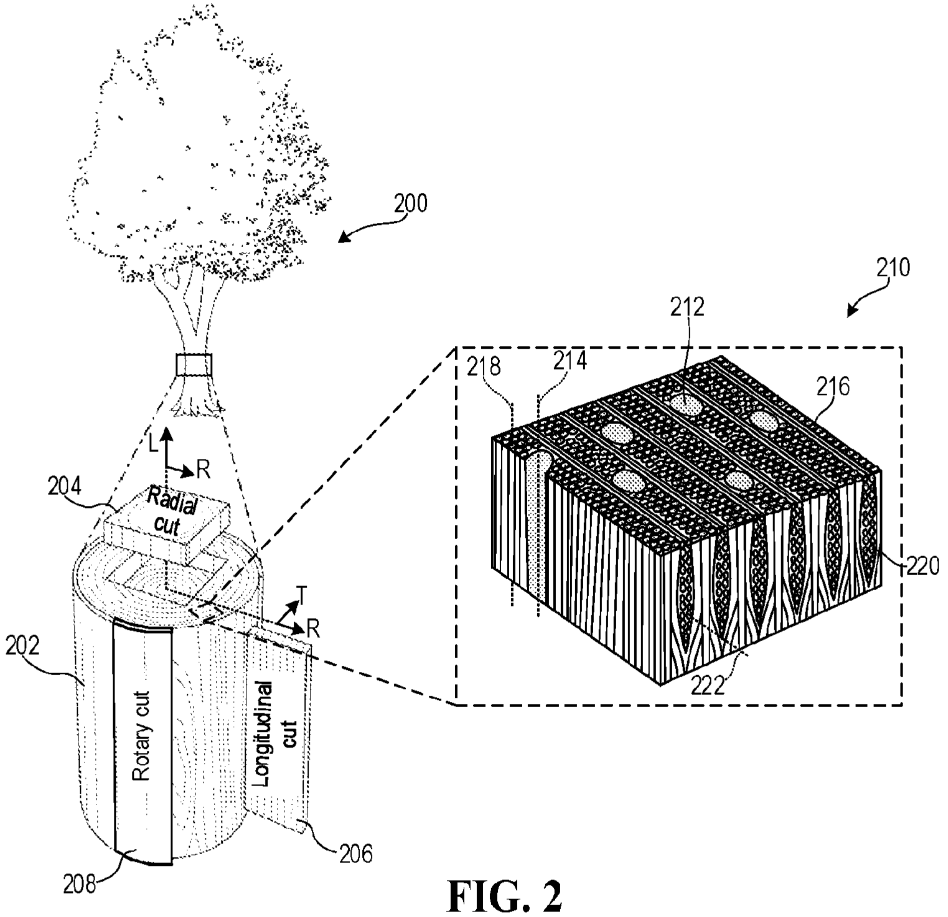
200
210
212
218
214
216
L
R
204
Radial cut
220
T
R
202
222
Rotary cut
Longitudinal cut
206
208

FIG. 2

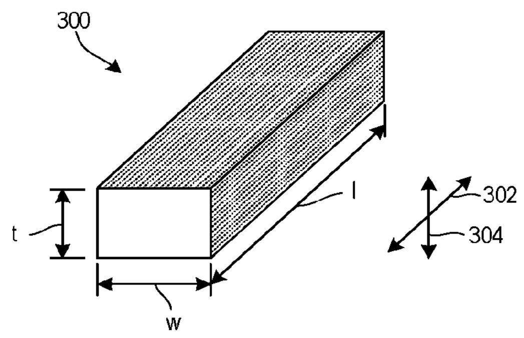
300
t
l
w
302
304

FIG. 3A

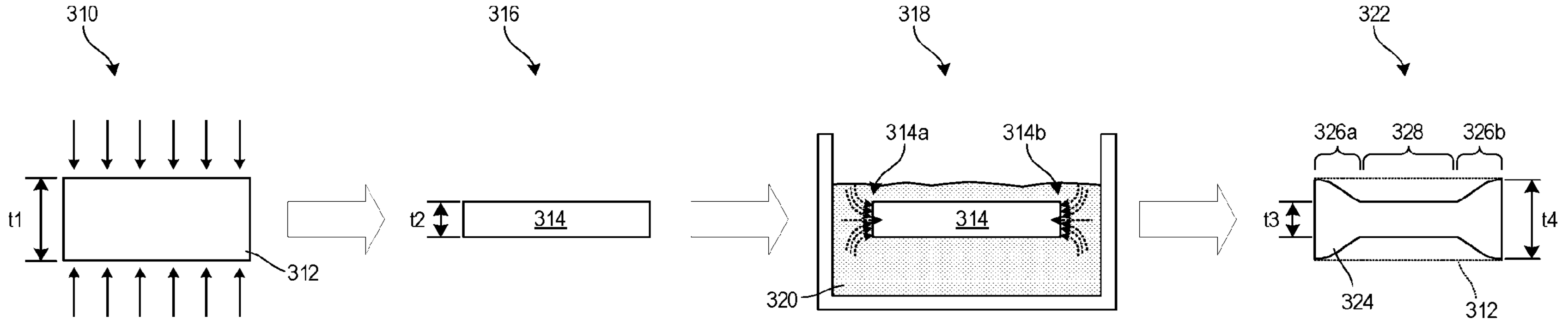
310
t1
312
316
t2
314
318
314a
314b
314
320
322
326a
328
326b
t3
t4
324
312

FIG. 3B

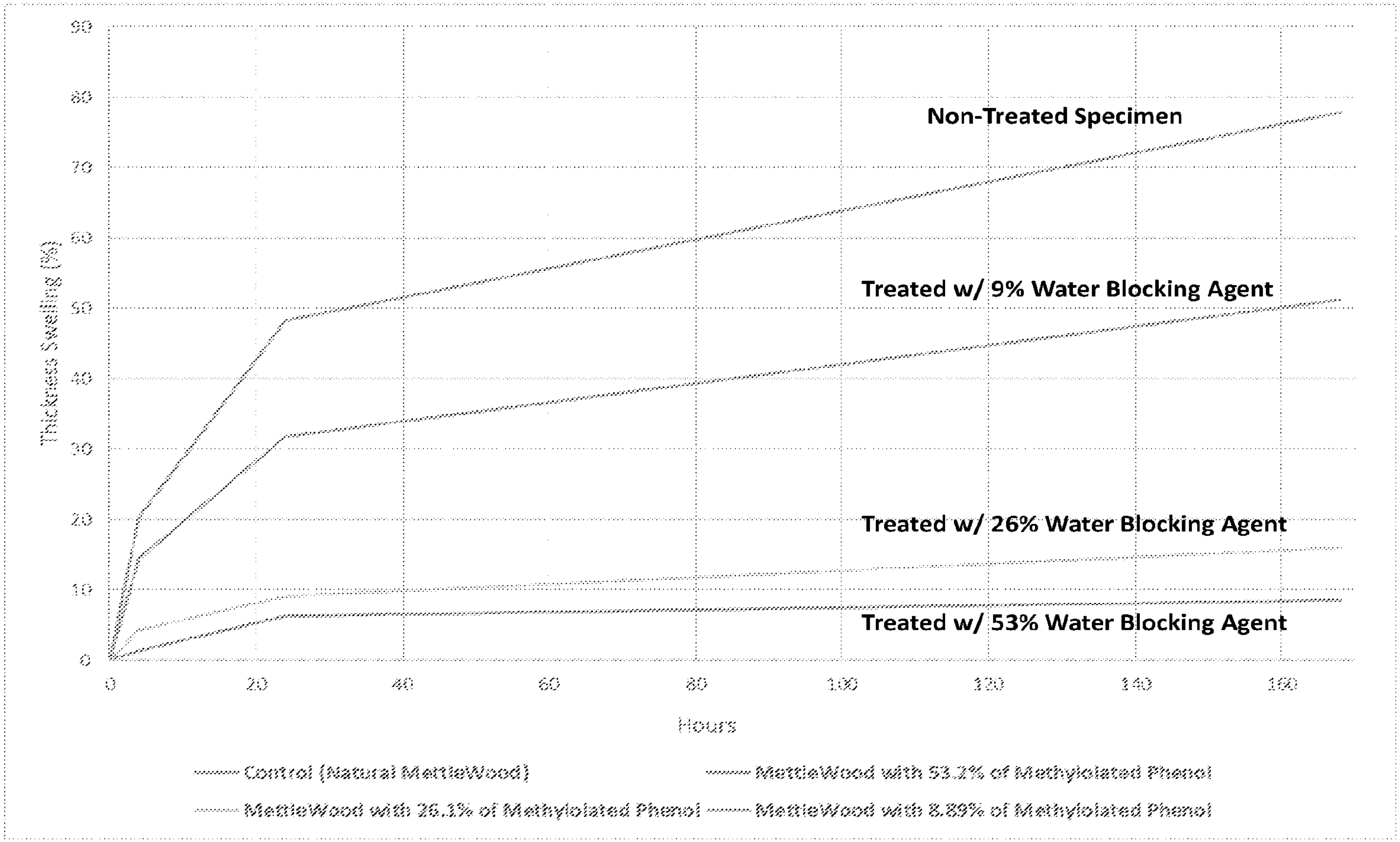
Thickness Swelling (%)
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
Hours
Non-Treated Specimen
Treated w/ 9% Water Blocking Agent
Treated w/ 26% Water Blocking Agent
Treated w/ 53% Water Blocking Agent
Control (Natural MettleWood)
MettleWood with 53.2% of Methylolated Phenol
MettleWood with 26.1% of Methylolated Phenol
MettleWood with 8.89% of Methylolated Phenol

FIG. 4

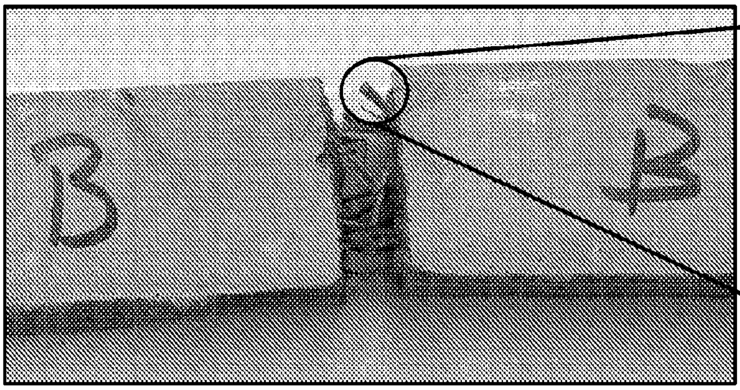

FIG. 5A

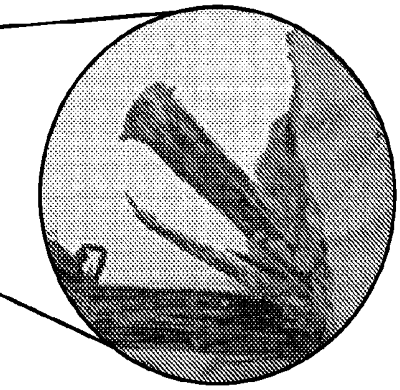

FIG. 5B

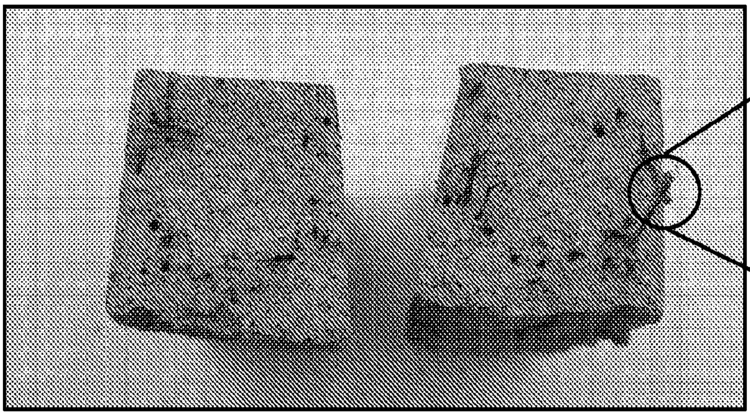

FIG. 5C

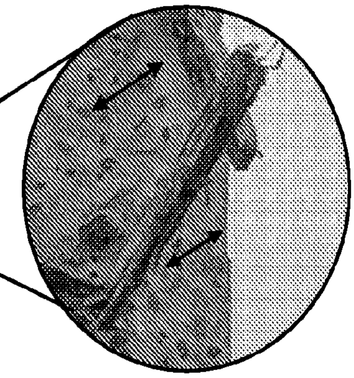

FIG. 5D

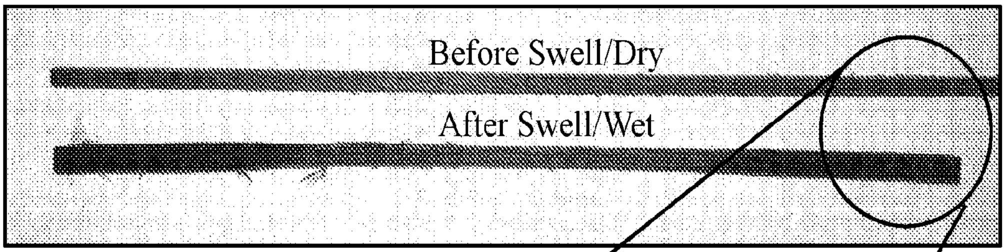

FIG. 6A

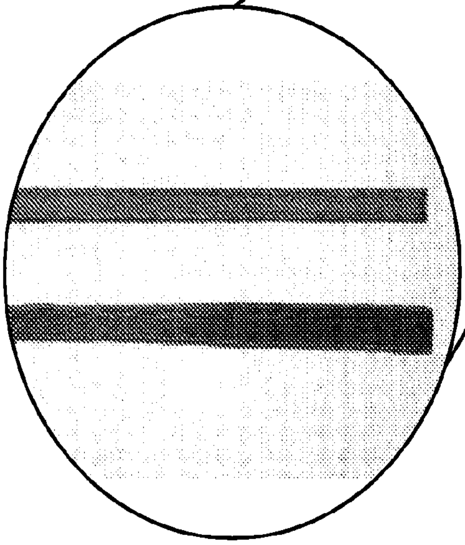

FIG. 6B