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(54) Title: PLANT MATERIALS WITH IMPROVED WATER STABILITY, AND METHODS FOR FABRICATION THEREOF

(57) Abstract: A plant material can be infiltrated with a solution having stabilizing agent and/or stabilizing agent precursors. The stabilizing agent and/or precursors can be absorbed within amorphous cellulose and/or hemicellulose regions of cell walls of the plant material. After the infiltrating, the amorphous cellulose and/or hemicellulose can be crosslinked with the stabilizing agent. The stabilizing agent precursors can include a nucleophile and an electrophile, and the stabilizing agent can include a reaction product of the nucleophile and the electrophile. During the infiltrating, each of the stabilizing agent and/or the precursors can have a molecular weight less than or equal to 500 g/mole. After the crosslinking, the stabilizing agent can imbue the plant material with improved water stability, in particular, such that swelling of the plant material is limited regardless of a duration of exposure to water and/or an amount of water absorbed by the plant material.

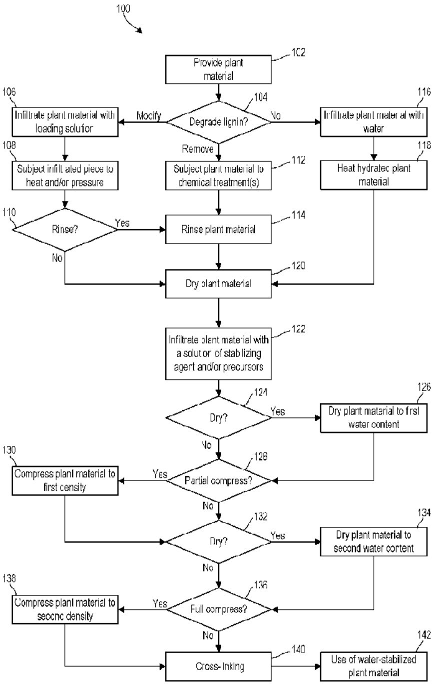

FIG. 1

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PLANT MATERIALS WITH IMPROVED WATER STABILITY, AND METHODS FOR FABRICATION THEREOF

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. 63/460,736, filed April 20, 2023, entitled "High Density Wood Compositions Made with Methylolated Phenol for Improved Water Resistance," 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 methods of fabricating plant materials with improved water stability.

BACKGROUND

Conventional wood products, including solid-sawn lumber and laminated veneer lumber, can have a density of about 300-800 kg/m^3, a tensile strength of about 100 MPa (strong axis), a modulus of about 11 GPa (strong axis), and a compressive strength of about 50 MPa (strong axis). Conventional wood products are readily available and are commonly used in building applications, especially residential construction. Steel is also used in construction. In comparison to wood, steel can have a density of about 7,800-8,000 kg/m^3, a tensile strength of about 400 MPa at yield, a modulus of about 200 GPa, and a compressive strength of about 170 MPa.

Although steel is stronger than conventional wood, production of each cubic meter of lumber is associated with about 110 kg of emitted carbon, while production of each cubic meter of steel is associated with about 12,000 kg of emitted carbon. Thus, there is a desire to replace steel with wood. This substitution strategy becomes more feasible when novel modification technologies, including densification, are used to increase the strength of wood.

In addition to strength, it is also important for building materials to be dimensionally stable. Steel is more dimensionally stable than conventional wood with respect to water exposure events, such as rain or floods. Steel does not absorb water and it does not swell when exposed to water. Unfortunately, when structures formed of conventional plant materials, such as wood, are exposed to water, they can absorb significant amounts of water (e.g., as much as the dry weight of the plant material). Most conventional plant material products also exhibit significant levels of swelling as they absorb water, for example, greater than ~20%. In some cases (e.g., with high-density plant material products), the amount of swelling can prevent adjacent components within a building structure from fitting together properly. This condition can increase the labor and complexity of the construction process. For example, when conventional wooden building materials are exposed to water in existing buildings (e.g. floods), the resulting swelling can sometimes be irreversible and can necessitate repairs.

Although many coatings and sealants exist for improving the water-resistance of wood and other plant materials, these coatings and sealants generally operate by creating a layer on the outer surface of the material. In many cases, these coatings are hydrophobic and effectively slow down the rate at which water absorbs into the treated material. However, if the exposure to water is sufficiently long, then the plant material will fully hydrate and swell. In addition, as swelling occurs, the applied coating can crack and/or detach from the plant material surface. While oils (e.g., tung oil, alkyd resins, etc.) have been used on wood to improve water resistance, these oils are limited in their ability to effectively absorb into critical regions of the plant material anatomy that are responsible for swelling, due at least in part to the hydrophobic nature of the oils. Indeed, while such absorbed oils can slow down the water absorption event, the treated plant materials will nevertheless eventually fully hydrate and swell if exposed to water for a sustained period of time.

Aspects of the disclosed subject matter may address one or more of the above-noted problems and disadvantages, among other things.

SUMMARY

Aspects of the present disclosure provide compressed plant materials with improved resistance to swelling in the presence of water, and methods for fabricating such plant materials. The plant material can be modified by homogeneous absorption of stabilizing agent precursors that penetrate the cross-section of the plant material. In some aspects, the stabilizing agent precursors can be transferred to specific regions of the plant material (e.g., amorphous cellulose and/or hemicellulose) that can potentially be swollen with water. Upon reaching the specific regions, the precursors can react to form stabilizing agents. In some aspects, the stabilizing agents formed from such stabilizing agent precursors can react with (e.g., crosslink) components in the specific regions in a manner that significantly reduces the water swelling potential after the plant material has been compressed to a target density (e.g., greater than 900 kg/m^3). In some aspects, the compressed plant material can comprise an array of mostly aligned, collapsed cells, wherein specific regions of the cells are crosslinked, and wherein the cells are distributed within a matrix of lignin (e.g., native and/or degraded lignin), wherein the lignin has also been crosslinked. In some aspects, the water-stabilized plant materials can have exceptional strength and exhibit a unique combination of high water absorption capacity and relatively low thickness swell potential (e.g., $< 10\%$, such as $\leq 5\%$).

In some aspects, the water-stabilized plant materials can be formed via a multi-step process. For example, in a first step of some aspects, sections of plant material (e.g., wood, such as lumber or veneer) that have a thickness direction that is generally aligned with the radial, tangential, or mixtures of radial and tangential directions of the plant material, can be modified by infiltrating the plant material with a loading solution. In some aspects, lignin in the plant material is partially degraded by the loading solution. Such degradation can facilitate subsequent compression of the plant material without breaking cells or fracturing the lignin (or at least reducing any breaking or fracturing). In some aspects, a portion of the lignin can also be removed from the plant material in the first step. Alternatively, in some aspects, the loading solution comprises water, and the plant material is heated to a temperature greater than about 50 °C after treatment with the loading solution.

In some aspects, a second step can comprise partially drying the treated plant material, for example, such that the moisture content of the treated plant material after drying is about 1-10% based on the dry weight of the treated plant material. In some aspects, a third step can comprise infiltrating the treated plant material with a stabilizing agent and/or precursors thereof under conditions suitable for transfer of the stabilizing agent and/or precursors thereof into the amorphous regions of the cellulose and/or hemicellulose regions of the treated plant material, wherein the selective absorption process occurs throughout the entire (or at least 90%) of the cross-section of the plant material. In some aspects, the time associated with the infiltration process can be sufficient for the concentration gradients of stabilizing agent and/or precursors thereof within the plant material to reach a state of equilibration. In some aspects, the infiltration is conducted under conditions that do not cause the stabilizing agent, formed by reactions of the precursors, to crosslink the cellulose and/or hemicellulose.

In some aspects, a fourth step can comprise partially drying the plant material without causing the stabilizing agent and/or precursors thereof to crosslink the cellulose and/or hemicellulose, while achieving a moisture content of the treated plant material after drying of about 1-25% based on the dry weight of the treated plant material. In some aspects, a fifth step can comprise subjecting the treated plant material to pressure (e.g., sustained pressure) along the axis that is parallel to the thickness direction of the plant material, for example, until the density of the plant material has been increased (e.g., to a value greater than about 900 kg/m^3). In some aspects, the compression of the plant material in the fifth step is performed without causing the stabilizing agent and/or precursors thereof to crosslink plant material and/or such that the partially compressed plant material has a moisture content in the range of about 1-20%.

In some aspects, a sixth step can comprise further drying the plant material without causing the stabilizing agent and/or precursors thereof to crosslink plant material, for example, such that the moisture content of the treated plant material is reduced to a value that is less than 10%. In some aspects, a seventh step can comprise subjecting the treated plant material to pressure (e.g., sustained pressure) along the axis parallel to the thickness direction of the treated plant material, for example, until the density of the plant material has been increased (e.g., to a value greater than about 1200 kg/m^3, for example, in a range of about 1,250 – 1,450 kg/m^3). In some aspects, the stabilizing agent can crosslink specific regions of the plant material, such as amorphous cellulose, hemicellulose, and/or lignin (e.g., previously degraded or native lignin), subsequent to compressing the plant material to a targeted density range (e.g., during the seventh step or after the seventh step). Alternatively or additionally, in some aspects, the fifth and sixth steps can be omitted.

In some aspects, the densified plant material, crosslinked in specific locations with stabilizing agent therein, can have density values in the range of about 900-1,450 kg/m^3 and can exhibit a capacity to absorb about 10-30% of the dry weight of the densified plant material in water, for example, without swelling greater than about 10% along the compressed direction.

In one or more aspects, a method can comprise infiltrating a plant material with a solution comprising stabilizing agent and/or stabilizing agent precursors, such that the stabilizing agent and/or stabilizing agent precursors are absorbed within amorphous cellulose and/or hemicellulose regions of cell walls of the plant material. The method can further comprise, after the infiltrating, crosslinking the amorphous cellulose and/or hemicellulose with the stabilizing agent. The stabilizing agent precursors can comprise a nucleophile and an electrophile. The stabilizing agent can comprise a reaction product of the nucleophile and the electrophile, or in some aspects, can simply be a product of a reaction between a nucleophile and an electrophile. During the infiltrating event, each of the stabilizing agent and precursors thereof can have a molecular weight less than or equal to 500 g/mole.

In one or more aspects, a structure can comprise a plant material and a stabilizing agent. The plant material can have cell walls with amorphous cellulose and/or hemicellulose regions. The stabilizing agent can crosslink the amorphous cellulose and/or hemicellulose regions of the cell walls of the plant material. The stabilizing agent can be a reaction product of a nucleophile and an electrophile. Each of the nucleophile, the electrophile, and the stabilizing agent can have a molecular weight less than or equal to 500 g/mole prior to crosslinking.

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. 1 is a simplified process flow diagram illustrating a method for fabricating plant materials with improved water stability, according to one or more aspects 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 water stabilization treatment, according to one or more aspects of the disclosed subject matter.

FIGS. 3A-3B are graphs of thickness swell (%) versus water absorption (%) for compressed poplar wood samples with and without stabilizing agent, respectively.

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*) or 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) or straw (e.g., formed from processed remains of cereal plants, such as rice, wheat, millet, or maize).

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 to 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, at least 0.9 g/cm^3, such as at least 1.1 g/cm^3 or even at least 1.2 g/cm^3 (e.g., 1.2-1.4 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 is a component of an engineered plant material structure with multiple constituent pieces (e.g., layers or chips) coupled together via an adhesive or other coupling agent (e.g., filler, such as carboxymethyl cellulose (CMC)), such as but not limited to cross-laminated timber (CLT), glued laminated timber (glulam) or bamboo (glubam), laminated veneer lumber (LVL), oriented strand board (OSB), parallel strand lumber (PSL), and/or oriented structural straw board (OSSB).

Fiber direction: A direction 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 fiber direction may be generally vertical or correspond to a direction of its water transpiration stream. This is in contrast to the radial direction, which extends from a center portion of the stem of a plant outward and is perpendicular to the fiber direction.

Polymerization: A chemical process by which monomers and/or oligomers react to form a polymer.

Crosslinking: A chemical process by which a small reactive molecule (e.g., less than 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 the freedom of motion of the polymer or macromolecule on a molecular level. In some aspects, crosslinking of amorphous cellulose and/or hemicellulose (e.g., via a stabilizing agent) can prevent volumetric expansion of the polymer as it absorbs water. Alternatively or additionally, in some aspects, crosslinking can cause lignin molecules (e.g., degraded lignin) 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 a nucleophile (e.g., Lewis base) and an electrophile (e.g., Lewis acid). In some aspects, the reaction product can be a product of a reaction wherein all atoms present in the reactants are maintained in the reaction product. In other aspects, the reaction product can be a product of a reaction wherein not all atoms present in the reactants are present in the reaction product. In some aspects, the reaction product can be an adduct. In some aspects, the reaction product has a molecular weight less than or equal to 500 g/mole.

Thickness: A cross-sectional dimension of a piece of plant material that is aligned with the direction of compression 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 of the plant material. In other aspects, the thickness dimension is aligned with the tangential direction 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 fiber and radial directions. In some aspects, the thickness direction corresponds to a minimum cross-sectional dimension of the piece of plant material.

Stabilizing Agent: The product of the reaction between the nucleophile and electrophile precursors. In some aspects, the stabilizing agent is formed from the reaction of a 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 stabilizing agent is a small molecule (e.g., less than 500 g/mole) that is hydrophilic. In certain aspects, the stabilizing agent can be highly water soluble. In some aspects, the stabilizing agent has the potential to crosslink lignin (e.g., degraded) within the plant material.

Stabilizing Agent Precursors: Chemical species that can be reacted to form a stabilizing agent. In some aspects, the stabilizing agent precursors comprise an electrophile and a nucleophile. In certain aspects, the stabilizing 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).

Introduction

Disclosed herein are compressed plant materials with improved resistance to swelling in the presence of water, and methods for fabrication of said plant materials. The disclosure is based on the counter-intuitive approach of making plant materials (e.g., wood) resistant to the swelling effects of water by treating it with compounds that share some of the same characteristics of water. While most technologies that are designed to reduce swelling in wood involve application of hydrophobic substances to the wood, aspects of the disclosed subject matter provide a more effective solution by treating the wood (or other plant material) with hydrophilic substances. aspects of the disclosed subject matter can be particularly effective at controlling excessive swelling in compressed plant material products. Because wood, and most other plant materials, exhibit "shape-memory" properties, their swell potential is especially large when they are compressed during their manufacturing process. While plant materials, including wood, typically exhibit about 2-8% of swell in their radial or tangential axes when their water levels are changed from a dry state to a fully saturated state, compressed plant materials can exhibit more than 30% swell when changed from a dry state to a fully saturated state. Typically, swell values are greater when the plant materials are compressed to a greater extent. With attempts to increase the strength of wood by compressing it to higher density values (e.g., in the range of 900-1450 kg/m^3), the ability to inhibit, or at least reduce, swelling in the presence of water can be important.

While not wishing to be bound by theory, it is instructive to note that when water is absorbed into conventional wood (or other plant materials), 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. Relatively little absorption of the water occurs in the lignin-based regions of the wood. Likewise, very little water absorbs into the crystalline cellulose regions of the wood. Furthermore, until the cell wall becomes saturated (for conventional wood, at an absorbed water mass of about 28-30% of the dry wood), the water does not transfer into the cell lumens, although the lumens can absorb water after the cell wall has been saturated. More than 90% of the swelling in conventional solid wood that occurs when the wood becomes wet can be attributed to swelling of the cell wall. Filling the lumens in the wood (or other plant material) with water is typically associated with very little dimensional change in the solid wood.

The stabilizing agent and the stabilizing agent precursors described herein are unique at least in the context of their use in methods according to aspects of the present disclosure. The stabilizing agent and the stabilizing agent precursors according to aspects of the present disclosure are typically small in size, hydrophilic, and/or have a desired level of water solubility (e.g., high water solubility as described herein). Such properties, individually or in combination, allows these compounds to be transferred to the specific regions of the plant material that are responsible for most of the swelling under conditions of water exposure. In some aspects, after diffusing the stabilizing agent and/or precursors to the most active sites in the plant tissue, the material is compressed, and subsequent to compression (or during a final compression stage in some aspects), the stabilizing agent crosslinks the amorphous cellulose and/or hemicellulose in a manner that prevents volumetric expansion of these polysaccharides. Thus, the reaction rate kinetics of the stabilizing agent and the process conditions are controlled such that the stabilizing agent is activated (e.g., to crosslink) only after the wood (or other plant material) has achieved its final compressed state.

In some aspects, compression of the plant material can be facilitated by partial degradation of the lignin prior to compression. In such aspects, a secondary function of the stabilizing agent can be to crosslink the residual degraded lignin after compression has been achieved. This crosslinking of the degraded lignin can help reduce the presence of extractives in the final product.

In some aspects, compressed plant material comprising amorphous cellulose and/or hemicellulose, which were infiltrated with the stabilizing agent before compression and crosslinked with the stabilizing agent after compression, retain some water absorption capacity, but exhibit substantially reduced swelling potential, for example, along the compression direction (e.g., parallel to the thickness dimension). For example, the swelling along the thickness direction of the plant material that has been treated with stabilizing agent according to aspects of the disclosed subject matter can be limited to no more than 10% (e.g., ≤ 5%) regardless of the amount of water absorbed the plant material or the duration of water exposure. This characteristic, in combination with the very small size of the stabilizing agent and stabilizing agent precursors, promotes spontaneous transfer of these molecules to sites in the plant material microstructure that preferentially absorb and hold water.

Fabrication Method Examples

FIG. 1 illustrates aspects of a method 100 for fabricating a plant material, or a structure comprising a plant material, with improved water stability. 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. 1, 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, the relevant portion of which is incorporated herein by reference) and/or lignin modification (for example, using the lignin modification process described in U.S. Publication No. 2024/0083067, the relevant portion of which is incorporated herein by reference).

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 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 used in aspects of the method described herein 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. In some aspects, the loading solution comprises $NaHSO_3$ and/or Na_2SO_3. 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). In some particular aspects, the loading solution includes NaOH, LiOH, KOH, Na_2O, or any combination thereof. Additional exemplary combinations of chemicals in certain aspects of the disclosed method 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_2S_x, any of the foregoing with NaOH replaced by LiOH or KOH, or any combination of the foregoing. In some aspects, the loading solution comprises $NaHSO_3$ and/or Na_2SO_3, which can be formed by certain loading solution chemicals. 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.

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. 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 stabilizing agent precursors and/or stabilizing agent. The stabilizing agent precursors can comprise a nucleophile and an electrophile, and the stabilizing agent can comprise a reaction product of the nucleophile and the electrophile. Each of the stabilizing agent precursors can have a molecular weight less than or equal to 500 g/mole, such that, during the infiltrating, the stabilizing agent precursors become absorbed within amorphous cellulose and/or 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 stabilizing agent, the stabilizing agent can also have a molecular weight less than or equal to 500 g/mole, such that, during the infiltrating, the stabilizing agent becomes absorbed within amorphous cellulose and/or 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, or any combination of an oxirane, oxazolidine, or bisoxazolidine with the aldehyde.

In some aspects, the nucleophile is phenol, the electrophile is formaldehyde, and the stabilizing agent is methylolated phenol. For example, in some aspects, the stabilizing 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 stabilizing agent can be highly soluble in water, which can promote spontaneous transfer of these compounds to the amorphous cellulose and/or hemicellulose regions of the cell wall during the infiltration process.

In some aspects of the disclosure, the stabilizing agent is highly hydrophilic. In some aspects, the stabilizing agent can be water soluble, under alkaline conditions, neutral conditions, or both. In certain aspects, the stabilizing 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 stabilizing 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/or hemicellulose regions in the plant cell walls. Thus, crosslinking of the amorphous cellulose and/or hemicellulose regions in the plant cell walls could not be achieved by employing dispersed, suspended, or emulsified compounds.

In some aspects, the stabilizing agent has the potential to crosslink the plant material tissue (amorphous cellulose and/or hemicellulose). The selection of the stabilizing 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/or 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 stabilizing agent precursors can be (i) mixtures of nucleophiles and electrophiles, (ii) reaction products of nucleophiles and electrophiles, and/or (iii) 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 and mass spectroscopy.

In some aspects of the disclosure, the stabilizing agent precursors are highly hydrophilic. In particular aspects disclosed herein, the stabilizing 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 stabilizing 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 another example, a suitable bisoxazolidine is 5-hydroxymethyl-1-aza-3,7-dioxabicyclo [3,3,0] octane.

In some aspects, stabilizing agents can include low-molecular-weight reaction products obtained by reacting the aforementioned nucleophiles and electrophiles. Examples of suitable reaction products 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, stabilizing 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 stabilizing 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 stabilizing agent can comprise more than one nucleophile and/or more than one electrophile. The water content of the solution containing stabilizing agent precursors and/or stabilizing 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, stabilizing agents can be prepared by reacting nucleophiles and electrophiles together to form low-molecular-weight reaction products. 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, 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 50-80° C until samples of the mixture have a viscosity of about 20-35 cPs at a temperature of 20° C. Such a determination can be made by use of Gardner-Holdt bubble tubes or other methods of viscosity measurement. During this final stage of reaction time, formaldehyde can continue to add to the phenol as methylol groups. A modest level of oligomer formation can also occur during this extended period of heating. Oligomers can be formed within the mixture and can be comprised of two or three substituted phenol groups that are bonded together through ether linkages. Oligomer formation must not be allowed to proceed to the point of forming reaction products with a molecular weight of 500 g/mole or higher. Upon achieving the viscosity target, the mixture can be rapidly cooled to room temperature. In some aspects, urea can be added to the mixture at the later stages of the production process (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 to improve the water solubility of the reaction products. 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 stabilizing agent. In other aspects, the resulting mixture can be further formulated with water, nucleophile(s), or electrophile(s) to obtain the stabilizing 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/or hemicellulose. 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/or 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 Da. Likewise, the molecular weight of molecules in "green phenolic resins" are typically about 800-1,500 Da. Thus, the molecules in green phenolic resins are also too big to effectively diffuse into the critical regions of the plant tissue that are most prominently associated with swelling in the presence of water.

In some aspects, one or more sections of treated plant material can be immersed in an aqueous solution with stabilizing agent and/or stabilizing agent precursors. The system 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 throughout the entire cross-section of the plant material. In another aspect, the treated plant material and aqueous solution are loaded into a pressure vessel and the mixture is subjected to positive pressure, wherein the gauge pressure is in the range of about 100-4,500 MPa and the temperature is maintained at about 20-50° C.

The absorption process is continued for a period of time that is sufficient to achieve distribution of the stabilizing agent (and/or precursors thereof) throughout the entire cross-section of the treated plant material. In contrast, it would not be sufficient to absorb the stabilizing agent (and/or precursors thereof) only into the outer surface of the treated plant material, and procedures that result in this condition are outside of the scope of the present disclosure. The soaking time required to achieve absorption of the stabilizing 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 stabilizing agent and/or stabilizing 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 stabilizing agent.

During the stabilizing 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 10-80%. The amount of absorbed stabilizing agent solute or absorbed stabilizing agent precursor solute can be about 1-30% of the dry mass of the wood.

The method 100 can proceed to decision block 124, where it is determined if the plant material infiltrated with the solution of stabilizing agent precursors or stabilizing 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 stabilizing agent to prematurely crosslink the amorphous cellulose and/or hemicellulose before the plant material has been compressed to the targeted level. Appropriate drying conditions will be dependent upon the specific stabilizing agent composition or stabilizing 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 of about 60-80° C for a period of about 6-10 hours. Drying the plant material for this period of time without crosslinking the amorphous cellulose and/or hemicellulose can be achieved by selection of a stabilizing agent with a relatively high energy of activation value. For example, stabilizing 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 1-20%.

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 and/or hemicellulose by action of the stabilizing 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 °C and about 160 °C, e.g., greater than or equal to 100 °C. 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 stabilizing 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., ≥ 1.1 g/cm^3 or ≥ 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 20-150° 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 900-1,250 kg/m^3. This compression process can take about 15-100 minutes depending on the original thickness of the plant material, the applied pressure, the temperature of the platens, the wood species, and other factors including those related to the lignin degradation step (first step) in the process. There is an economic incentive to conduct the compression step as rapidly as possible, but slower compression rates can yield finished products with improved surface quality (less cracking). In some aspects, plasticized compression without fracturing the plant material can be achieved by partial modification of the lignin (and/or hemicellulose), for example, via process blocks 106-108, and/or partial removal of the lignin, for example, via process blocks 112-114. 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 stabilizing agent solute molecules do not prematurely crosslink the amorphous cellulose and/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 stabilizing agent solute molecules (or precursors thereof) do not crosslink the amorphous cellulose and/or 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. 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 stabilizing agent (or precursors thereof) does not prematurely crosslink the amorphous cellulose and/or hemicellulose during this step.

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 1200-1450 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 1,250-1,450 kg/m^3, inclusive. Subsequent to achieving the targeted level of compression, the absorbed stabilizing agent solute molecules can crosslink the amorphous cellulose and/or hemicellulose in manner that significantly prevents them from undergoing volumetric expansion in the presence of water.

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 100-200° 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 1,200-1,450 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 1,300 kg/m^3, for example, at least 1,350 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 manufacturing 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/or 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/or 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/or hemicellulose are crosslinked with stabilizing agent within the plant material. For example, after complete compression of the plant material has been achieved, the amorphous cellulose and/or hemicellulose can be crosslinked via the stabilizing agent such that they are not able to undergo significant levels of volumetric expansion in the presence of water. In some aspects, after achieving the targeted level of compression, the plant material can be heated further until crosslinking of the amorphous cellulose and/or 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/or 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 1,200-1,450 kg/m^3 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. In some aspects, the plant material can be restrained in the kiln in order to prevent, or at least reduce, the formation of geometric defects, such as twist or warpage.

After crosslinking, the method 100 can proceed to process block 142, where the water-stabilized plant material can optionally be machined, cut, transported, assembled, and/or otherwise physically manipulated in preparation for eventual use. Machining processes can include, but are not limited to, cutting (e.g., sawing), drilling, woodturning, tapping, boring, carving, routing, sanding, grinding, and abrasive tumbling. Manipulating process can include, but are not limited to, bending, molding, and other shaping techniques. In some aspects, one or more pieces (e.g., thin sections) of the resulting dimensionally-stable, densified plant material can be laminated to one another or to other pieces or composites. For example, laminated veneer lumber or other composites can be made by laminating one or more sections of the resulting dimensionally-stable, densified wood. Lamination can be accomplished by use of, for example, phenolic, isocyanate, polyurethane, or epoxy-based adhesives.

In some aspects, process block 142 can also include use of the plant material as a structural member (e.g., a load bearing component or a non-load bearing component), such as a building component. For example, the laminates or composites including water-stabilized plant materials can be used as beams or other structural members, such as in residential or commercial buildings. When used in an environment where it is exposed to water, the swelling of the plant material with crosslinked amorphous cellulose and/or hemicellulose therein can be limited to 10% (along a thickness direction of the plant material) regardless of the duration of water exposure or the amount of water absorbed by the plant material. One of ordinary skill in the art will readily appreciate that the high-density, water-stabilized plant materials disclosed herein can be readily adapted for use in various applications based on the teachings of the present disclosure.

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 plant starting 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 stabilizing agent as described herein. Specifically, the disclosed method of preparation results in high-density plant material products with substantially reduced swelling potential, but with a retained level of water absorption capacity. The latter property can allow the modified plant material product to successfully interact with water-based adhesives, paints, and other coatings, for example, by absorbing water from the paint, coating, or adhesive. Alternatively or additionally, composites, such as laminated veneer lumber, can be manufactured using modified veneer that has been made in accordance with the present disclosure, wherein the composite is made using conventional water-based phenolic adhesives.

Although blocks 102-142 of method 100 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 have been separately illustrated and described, in some aspects, process blocks may be combined and performed together (simultaneously or sequentially). Moreover, although FIG. 1 illustrates a particular order for blocks 102-142, 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. 1. Alternatively or additionally, in some aspects, method 100 may comprise only some of blocks 102-142 of FIG. 1.

Fabricated Examples and Experimental Results

COMPARATIVE EXAMPLE: COMPRESSED WOOD WITHOUT A STABILIZING AGENT

High-density wood was prepared without a stabilizing agent and the resulting product was subjected to a water soak test, the results of which are shown in FIG. 3A.

Poplar lumber sections (19.1 mm thick x 127 mm wide x 305 mm long, 2 count) with a dry specific gravity of about 0.45 and a moisture content of about 8% were submerged in 5.0% sodium hydroxide aqueous solution at a temperature of 20° C and a gauge pressure of 19.3 bar for a period of 18 hours. The soaked lumber sections were then heated at a temperature of 170° C and a gauge pressure of 4 bar for a period of 3 hours. The treated lumber sections were then dried to a moisture content of about 7% under ambient conditions (20° C and 0 gauge pressure) for a period of about 10 days. The sections were then placed in a hot press with a platen temperature of 132° C. For the first 14 minutes the press was closed, but the pressure was less than 10 psi. After this initial heating period, the pressure was increased to 2.07 MPa over a period of 1 minute. The sections were maintained at this pressure for a period of 24 minutes. The pressure was then increased to 5.10 MPa over a period of 1 minute. The sections were maintained at this pressure for a period of 5 minutes. The pressure was then increased to 5.56 MPa over a period of 44 minutes. The pressure on the sections was then completely relieved over a period of 1 minute. The sections were then transferred out of the hot press and into a cold press. The sections were then cold-pressed at a temperature of 40° C and a pressure of 1 MPa for a period of 15 minutes.

The compressed wood had a density of about 1.13 kg/m^3 and a thickness of 7.7 mm. Three replicate test specimens (7.7 mm thick x 15.5 mm wide x 100.5 mm long, each) were isolated from the compressed wood sections. The test specimens were subjected to initial measurements of mass and dimension (thickness, width, and length). The thickness measurements were conducted at the midpoint of each of the four edges of each specimen. Specimens were then submerged under 1" of water for a period 168 hours. Test specimens were retrieved from the water and were measured for mass and dimension after intermediate soak periods of 4 and 24 hours, and again after 168 hours. The soaking liquor had a dark purple color at the completion of this test. Water absorption values and thickness swell values were calculated in the following manner:

$$\text{Water Absorption (\%)} = (100\%)\frac{(Mass\ at\ Time,t - Initial\ Mass)}{Initial\ Mass}$$

$$\text{Thickness Swell (\%)} = (100\%)\frac{(Thickness\ at\ Time,t - Initial\ Thickness)}{Initial\ Thickness}$$

Table 1. Water Soak Test Results for Compressed Wood Prepared without Stabilizing Agent

Soak Time (h)	Average Water Absorption (%)	Average Thickness Swell (%)
0	0	0
4	6.2	7.2
24	14.0	14.6
168	31.0	32.0

FABRICATED EXAMPLE: COMPRESSED WOOD WITH A STABILIZING AGENT

High-density wood was prepared with a stabilizing agent and the resulting product was subjected to a water soak test, the results of which are shown in FIG. 3B.

Poplar lumber sections (19.1 mm thick x 127 mm wide x 305 mm long, 2 count) with a dry specific gravity of about 0.45 and a moisture content of about 8% were submerged in 5.0% sodium hydroxide aqueous solution at a temperature of 20° C and a gauge pressure of 19.3 bar for a period of 18 hours. The soaked lumber sections were then heated at a temperature of 170° C and a gauge pressure of 4 bar for a period of 3 hours. The treated lumber sections were then dried to a moisture content of about 7% under ambient conditions (20° C and 0 gauge pressure) for a period of about 10 days.

Sub-sections (17.0 mm thick x 20 mm wide x 100 mm long, 16 count) were cut from the larger treated sections of poplar.

Stabilizing agent solution was prepared in the following manner. Polyethylene bottles (500 mL capacity each, 18 count) were each charged with 89% phenol solution (aq) (110.0 g) and 0.10%

sodium carbonate solution (aq) (1.0 g). The bottles were tightly capped and were then shaken for 15 seconds. The bottles were further charged with 37% formaldehyde solution (aq) (60.0 g). The bottles were tightly capped and were then shaken for 30 seconds. The closed bottles were stored at a temperature of 20° C for a period of 6 hours. A second charge of 37% formaldehyde solution (aq) (60.0 g) was added to each bottle. The bottles were tightly capped and were then shaken for 30 seconds. The closed bottles were stored at a temperature of 20° C for a period of 15 hours. A third charge of 37% formaldehyde solution (aq) (60.0 g) was added to each bottle. The bottles were tightly capped and were then shaken for 30 seconds. The closed bottles were stored at a temperature of 20° C for a period of 6 hours. A fourth charge of 37% formaldehyde solution (aq) (60.0 g) was added to each bottle. The bottles were tightly capped and were then shaken for 30 seconds. The closed bottles were stored at a temperature of 20° C for a period of 15 hours. The calculated percent solids of the resulting solution was 53.2%. The solutions had a viscosity of less than 20 cPs at 20° C.

All of the sub-sections of treated poplar lumber were selected for treatment with the stabilizing agent. Each sub-section was wrapped in metal mesh and placed into a steel beaker (10 L capacity). The loaded beaker was then further charged with stabilizing agent such that all of the wrapped sub-sections of treated poplar were submerged. The loaded beaker was placed into a pressure vessel and subjected to positive pressure (5 bar, gauge pressure) at a temperature of 25° C for a period of 30 minutes. Under these conditions, the treated wood sections absorbed approximately their own weight in stabilizing agent. One of the treated sub-sections was cut transversely to obtain two pieces (17.0 mm thick x 20 mm wide x 50 mm long, each). The freshly cut surface was viewed and it was apparent that the stabilizing agent had penetrated through the entire cross-section of the wood.

The sub-sections were then placed in a hot press with a platen temperature of 132° C. For the first 14 minutes the press was closed, but the pressure was less than 10 psi. After this initial heating period, the pressure was increased to 2.07 MPa over a period of 1 minute. The sub-sections were maintained at this pressure for a period of 24 minutes. The pressure was then increased to 5.10 MPa over a period of 1 minute. The sub-sections were maintained at this pressure for a period of 5 minutes. The pressure was then increased to 5.56 MPa over a period of 44 minutes. The pressure on the sub-sections was then completely relieved over a period of 1 minute. The pressure was then increased to 5.56 MPa over a period of 1 minute. The sub-sections were maintained at this pressure for a period of 179 minutes. The pressure on the sub-sections was then completely relieved over a period of 1 minute. The sub-sections were then transferred out of the hot press and into a cold press. The sub-sections were then cold-pressed at a temperature of 40° C and a pressure of 1 MPa for a period of 15 minutes.

The compressed wood had a density of about 1.34 kg/m^3 and a thickness of 8.0 mm. Ten replicate test specimens (8.0 mm thick x 24 mm wide x 81 mm long, each) were isolated from the compressed wood sections. The test specimens were subjected to initial measurements of mass and dimension (thickness, width, and length). The thickness measurements were conducted at the midpoint of each of the four edges of each specimen. Specimens were then submerged under 1" of water for a period 168 hours. Test specimens were retrieved from the water and were measured for mass and dimension after intermediate soak periods of 4 and 24 hours, and again after 168 hours. The soaking liquor had a transparent and faint yellow color at the completion of this test. Water absorption values and thickness swell values were calculated in the following manner:

$$\text{Water Absorption (\%)} = (100\%)\frac{(Mass\ at\ Time,t - Initial\ Mass)}{Initial\ Mass}$$

$$\text{Thickness Swell (\%)} = (100\%)\frac{(Thickness\ at\ Time,t - Initial\ Thickness)}{Initial\ Thickness}$$

Table 2. Water Soak Test Results for Compressed Wood Prepared with Stabilizing Agent

Soak Time (h)	Average Water Absorption (%)	Average Thickness Swell (%)
0	0	0
4	2.9	1.1
24	7.3	6.3
168	14.2	8.6

The dry, unmodified poplar wood has a swell potential of about 4.6% in the radial direction and about 8.2% in the tangential direction. Thus, the compressed poplar wood without stabilizing agent exhibited a thickness swell value (32.0%) that was much greater than that of the non-modified wood. In contrast, the compressed poplar wood that was prepared with stabilizing agent exhibited a thickness swell value of only 8.6%, which is only slightly higher than that of non-modified poplar wood.

Both compressed wood types demonstrated an ability to absorb water, but the rate of water absorption in the sample type that was made with stabilizing agent was about 50% slower than that of the sample type that was prepared without stabilizing agent.

If we examine the relationship between water absorption and thickness swell for the compressed wood that was prepared without stabilizing agent, we observe a linear relationship with strong correlation between these two parameters ($R^2 = 0.985$) for soak time values of 4, 24 and 168 hours. The slope associated with this relationship is about 1.01 (see FIG. 3B).

In comparison, there is an approximately linear relationship between water absorption and thickness swell for the compressed wood that was prepared with stabilizing agent ($R^2 = 0.810$) for soaking time values of 4 or 24 hours only. The slope of this relationship is about 1.04, which is very similar to that associated with the compressed wood that was prepared with no stabilizing agent. When the soak time for the compressed wood that was prepared with stabilizing agent was 168 hours, the water absorption values were greater than 9%. When the water absorption values for this wood type were between 9.4 and 16.8%, the average thickness swell was only 8.6%. Thus, for this type of modified wood, the maximum thickness swell value (on average) appears to be about 8.6%. The thickness swell value of the compressed wood that was prepared without stabilizing agent was 32.0% after soaking for 168 hours. The maximum swell value could actually be greater than 32.0% for the compressed wood that was prepared without stabilizing agent, which might have been observed if the water soaking test had been conducted for a period longer than 168 hours.

Compressed wood made in accordance with the present disclosure has density values in the range of about 900-1,450 kg/m^3 and comprises collapsed wood cells based on cellulose and/or hemicellulose, wherein regions of the cell wall that specifically comprise amorphous cellulose and/or hemicellulose are crosslinked in manner that significantly reduces their ability to undergo volumetric swelling in the presence of water. Lignin that has been degraded, molded, and then crosslinked, exists as a continuous phase between the modified cells. Cell walls that have been infiltrated with the stabilizing agent have a color that is significantly darker than that of the cells prior to treatment. Evidence of the stabilizing agent treatment is most prominently demonstrated by the altered hydration and swelling behavior of the modified plant material, which has the capacity to absorb about 10-30% of the dry weight of the plant material in water, without swelling greater than about 10% along the compressed axis. This combined set of properties is of significant commercial value and has not previously been demonstrated.

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:

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

crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent after infiltrating the first plant material with the solution,

wherein (i) the stabilizing agent precursors comprise a nucleophile and an electrophile, and the stabilizing agent comprises a reaction product of the nucleophile and the electrophile, and (ii) each of the stabilizing agent and the stabilizing agent precursors has a molecular weight less than or equal to 500 g/mole when infiltrating the first plant material with the solution.

Clause 2. The method of Clause 1, wherein a level of swelling of the first plant material, with the stabilizing agent therein, along a thickness direction of the first plant material is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the first plant material.

Clause 3. The method of any of Clauses 1 or 2, 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; (iii) both the aldehyde and the oxirane; or (iv) both the aldehyde and the bisoxazolidine.

Clause 4. The method of any one of Clauses 1-3, 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 5. The method of any one of Clauses 1-4, wherein the nucleophile is phenol, the electrophile is formaldehyde, the stabilizing 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 6. The method of any one of Clauses 1-5, wherein a molar ratio of formaldehyde to phenol for the stabilizing agent precursors is in a range of 1:1 to 3:1, inclusive.

Clause 7. The method of any of Clauses 1-6, wherein:

(i) the solution comprises stabilizing 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 stabilizing agent and/or the stabilizing 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 8. The method of any one of Clauses 1-7, further comprising degrading a native lignin of an initial plant material so as to form the first plant material prior to infiltrating the first plant material with the solution, wherein degrading the native lignin comprises 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.

Clause 9. The method of any one of Clauses 1-8, wherein degrading the native lignin 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 10. The method of any one of Clauses 1-9, wherein the loading solution comprises sodium hydroxide, sodium sulfite, an oxidizing agent, or any combination of the foregoing.

Clause 11. The method of any one of Clauses 1-10, wherein the oxidizing agent comprises ozone, oxygen, hydrogen peroxide, or an organic peroxide.

Clause 12. The method of any one of Clauses 1-11, wherein the loading solution comprises water.

Clause 13. The method of any one of Clauses 1-12, 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 14. The method of any one of Clauses 1-13, 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 15. The method of any one of Clauses 1-14, wherein degrading the native lignin 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 16. The method of any one of Clauses 1-15, 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 17. The method of any one of Clauses 1-16, wherein the one or more chemical solutions comprise sodium hydroxide ($NaOH$), lithium hydroxide ($LiOH$), potassium hydroxide (KOH), sodium sulfite (Na_2SO_3), sodium sulfate (Na_2SO_4), sodium sulfide (Na_2S), urea (CH_4N_2O), NaH_2O_3, sulfur dioxide (SO_2), anthraquinone ($C_{14}H_8O_2$), 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), chorine (Cl_2), ozone (O_3), or any combination of the foregoing.

Clause 18. The method of any one of Clauses 1-17, wherein a lignin content of the first 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 19. The method of any one of Clauses 1-18, further comprising drying the first plant material to have a water content of 1-20 wt%, inclusive, after degrading the native lignin and prior to infiltrating the first plant material with the solution.

Clause 20. The method of any one of Clauses 1-19, further comprising:

infiltrating an initial plant material with a liquid comprising water prior to infiltrating the first plant material with the solution; and

subjecting the initial plant material, with the liquid therein, to a temperature of at least 50 °C.

Clause 21. The method of any one of Clauses 1-20, further comprising compressing the first plant material with the stabilizing agent and/or stabilizing agent precursors therein after infiltrating the first plant material with the solution.

Clause 22. The method of any one of Clauses 1-21, wherein the first plant material, with the stabilizing agent and/or stabilizing agent precursors therein, is compressed to have a first density of at least 900 kg/m^3.

Clause 23. The method of any one of Clauses 1-22, wherein compressing the first plant material, with the stabilizing agent and/or stabilizing agent precursors therein, is performed along a thickness direction of the first plant material, and a thickness of the first plant material after compression is no more than 50% of a thickness of the first plant material prior to compression.

Clause 24. The method of any one of Clauses 1-23, wherein the first density is in a range of 900-1200 kg/m^3, inclusive.

Clause 25. The method of any one of Clauses 1-24, wherein 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 26. The method of any one of Clauses 1-25, wherein compressing is performed at a temperature in a range of 20-60 °C.

Clause 27. The method of any one of Clauses 1-26, wherein compressing is performed such that the stabilizing agent and/or stabilizing agent precursors within the first plant material do not crosslink the amorphous cellulose and/or hemicellulose regions.

Clause 28. The method of any one of Clauses 1-27, further comprising drying the first plant material to a moisture content in a range of 15-25 wt%, inclusive, after infiltrating the first plant material with the solution and prior to compressing the first plant material.

Clause 29. The method of any one of Clauses 1-28, further comprising drying the first plant material to have a water content of 1-10 wt%, inclusive, after compressing the first plant material.

Clause 30. The method of any one of Clauses 1-29, wherein the water content of the first plant material after drying is about 5 wt%.

Clause 31. The method of any one of Clauses 1-30, further comprising further compressing the first plant material after drying the first plant material.

Clause 32. The method of any one of Clauses 1-31, wherein the first plant material is further compressed to have a second density of at least 1200 kg/m^3.

Clause 33. The method of any one of Clauses 1-32, wherein crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent occurs during further compressing the first plant material.

Clause 34. The method of any one of Clauses 1-33, wherein crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent occurs after further compressing the first plant material.

Clause 35. The method of any one of Clauses 1-34, wherein the second density is in a range of 1200-1450 kg/m^3, inclusive.

Clause 36. The method of any one of Clauses1-35, wherein 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 37. The method of any one of Clauses 1-36, wherein, during infiltrating the first plant material with the solution:

(i) the stabilizing agent is hydrophilic and has a water solubility such that at least 30g thereof dissolves in 100 mL of water at 20 °C;

(ii) the stabilizing agent precursors are hydrophilic and have a water solubility such that at least 2g thereof dissolves in 100 mL of water at 20 °C; or

(iii) a combination of (i) and (ii).

Clause 38. The method of any one of Clauses 1-37, wherein the amorphous cellulose and/or hemicellulose regions remain hydrophilic after being crosslinked.

Clause 39. The method of any one of Clauses 1-38, wherein an amount of stabilizing agent and/or stabilizing agent precursors absorbed within the cell walls of the first plant material after infiltrating the first plant material with the solution is in a range of 1-25 wt%, inclusive, of the first plant material in a dry state prior to infiltrating.

Clause 40. The method of any one of Clauses 1-39, wherein infiltrating the first plant material with the solution is performed at a temperature in a range of 20-50 °C, inclusive.

Clause 41. The method of any one of Clauses 1-40, further comprising infiltrating an initial plant material with a loading solution prior to infiltrating the first plant material with the solution comprising the stabilizing agent and/or the stabilizing agent precursors.

Clause 42. The method of any one of Clauses 1-41, wherein the loading solution and/or the solution comprising the stabilizing agent or the stabilizing agent precursors comprises water, sodium hydroxide, a catalyst, or any combination thereof.

Clause 43. The method of any one of Clauses 1-42, wherein the nucleophile is phenol or cresol, and the electrophile is an oxazolidine or a bisoxazolidine.

Clause 44. The method of any one of Clauses 1-43, wherein the first plant material is wood.

Clause 45. The method of any one of Clauses 1-44, wherein the first plant material is bamboo.

Clause 46. A structure formed by the method of any one of Clauses 1-45.

Clause 47. A structure comprising:

a plant material having one or more cell walls comprising an amorphous cellulose region and a hemicellulose region; and

a stabilizing agent crosslinking the amorphous cellulose region and/or the hemicellulose region of the one or more cell walls of the plant material to form a crosslinked plant material,

wherein the stabilizing agent is a reaction product of a nucleophile and an electrophile, and

each of the nucleophile, the electrophile, and the stabilizing agent have a molecular weight less than or equal to 500 g/mole prior to crosslinking.

Clause 48. The structure of Clause 47, wherein a level of swelling of the plant material, with the stabilizing agent therein, along a thickness direction of the plant material is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the plant material.

Clause 49. The structure of any one of Clauses 47-48, wherein:

the nucleophile comprises an aromatic nucleophile;

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

Clause 50. The structure of any one of Clauses 47-49, wherein:

(i) the aromatic nucleophile comprises phenol or cresol;

(ii) the electrophile is soluble in water and comprises formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, or glutaraldehyde; or

(iii) a combination of (i) and (ii).

Clause 51. The structure of any one of Clauses 47-50, nucleophile is phenol or cresol, and wherein the electrophile is an oxazolidine or a bisoxazolidine.

Clause 52. The structure of any one of Clauses 47-51, wherein at least a portion of a lignin in the plant material is modified as compared to a lignin of a native plant material.

Clause 53. The structure of any one of Clauses 47-52, 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 54. The structure of any one of Clauses 47-53, wherein a lignin content of the plant material is less than that in a native plant material.

Clause 55. The structure of any one of Clauses 47-54, wherein the crosslinked plant material has a density of at least 900 kg/m^3.

Clause 56. The structure of any one of Clauses 47-55, wherein the crosslinked plant material has a density of at least 1200 kg/m^3.

Clause 57. The structure of any one of Clauses 47-56, wherein the crosslinked plant material has a density in a range of 1200-1450 kg/m^3, inclusive.

Clause 58. The structure of any one of Clauses 47-57, wherein the plant material is a densified piece with native lumina formed by the one or more cell walls of the plant material that are substantially collapsed and cellulose-based fibers forming the cell walls being aligned along a common direction.

Clause 59. The structure of any one of Clauses 47-58, wherein (i) the stabilizing agent is hydrophilic, and/or (ii) the amorphous cellulose region and/or the hemicellulose region that is crosslinked with the stabilizing agent is hydrophilic.

Clause 60. The structure of any one of Clauses 47-59, wherein the stabilizing agent has a water solubility such that at least 2 g of the stabilizing agent dissolves in 100 mL of water at a temperature of 20 °C.

Clause 61. The structure of any one of Clauses 47-60, wherein the stabilizing agent has a water solubility such that at least 30 g of the stabilizing agent dissolves in 100 mL of water at a temperature of 20 °C.

Clause 62. The structure of any one of Clauses 47-61, wherein the plant material is wood.

Clause 63. The structure of any one of Clauses 47-62, wherein the plant material is bamboo.

Conclusion

Any of the features illustrated or described herein, for example, with respect to FIGS. 1-3B and Clauses 1-63, can be combined with any other feature illustrated or described herein, for example, with respect to FIGS. 1-3B and Clauses 1-63 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:

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

crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent after infiltrating the first plant material with the solution,

wherein (i) the stabilizing agent precursors comprise a nucleophile and an electrophile, and the stabilizing agent comprises a reaction product of the nucleophile and the electrophile, and (ii) each of the stabilizing agent and the stabilizing agent precursors has a molecular weight less than or equal to 500 g/mole when infiltrating the first plant material with the solution.

2. The method of claim 1, wherein a level of swelling of the first plant material, with the stabilizing agent therein, along a thickness direction of the first plant material is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the first plant material.

3. The method of claim 1, 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; (iii) both the aldehyde and the oxirane; or (iv) both the aldehyde and the bisoxazolidine.

4. The method of claim 3, 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).

5. The method of claim 1, wherein the nucleophile is phenol, the electrophile is formaldehyde, the stabilizing 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.

6. The method of claim 5, wherein a molar ratio of formaldehyde to phenol for the stabilizing agent precursors is in a range of 1:1 to 3:1, inclusive.

7. The method of claim 1, wherein:

(i) the solution comprises stabilizing 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 stabilizing agent and/or the stabilizing 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).

8. The method of claim 1, further comprising degrading a native lignin of an initial plant material so as to form the first plant material prior to infiltrating the first plant material with the solution, wherein degrading the native lignin comprises 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.

9. The method of claim 8, wherein degrading the native lignin 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.

10. The method of claim 9, wherein the loading solution comprises sodium hydroxide, sodium sulfite, an oxidizing agent, or any combination of the foregoing.

11. The method of claim 10, wherein the oxidizing agent comprises ozone, oxygen, hydrogen peroxide, or an organic peroxide.

12. The method of claim 9, wherein the loading solution comprises water.

13. The method of claim 9, 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.

14. The method of claim 9, 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.

15. The method of claim 8, wherein degrading the native lignin 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.

16. The method of claim 15, 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.

17. The method of claim 16, wherein the one or more chemical solutions comprise sodium hydroxide ($NaOH$), lithium hydroxide ($LiOH$), potassium hydroxide (KOH), sodium sulfite (Na_2SO_3), sodium sulfate (Na_2SO_4), sodium sulfide (Na_2S), urea (CH_4N_2O), NaH_2O_3, sulfur dioxide (SO_2), anthraquinone ($C_{14}H_8O_2$), 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), chorine (Cl_2), ozone (O_3), or any combination of the foregoing.

18. The method of claim 15, wherein a lignin content of the first 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.

19. The method of claim 8, further comprising drying the first plant material to have a water content of 1-20 wt%, inclusive, after degrading the native lignin and prior to infiltrating the first plant material with the solution.

20. The method of claim 1, further comprising:

infiltrating an initial plant material with a liquid comprising water prior to infiltrating the first plant material with the solution; and

subjecting the initial plant material, with the liquid therein, to a temperature of at least 50 °C.

21. The method of any one of claims 1, 8, or 20, further comprising compressing the first plant material with the stabilizing agent and/or stabilizing agent precursors therein after infiltrating the first plant material with the solution.

22. The method of claim 21, wherein the first plant material, with the stabilizing agent and/or stabilizing agent precursors therein, is compressed to have a first density of at least 900 kg/m^3.

23. The method of claim 21, wherein compressing the first plant material, with the stabilizing agent and/or stabilizing agent precursors therein, is performed along a thickness direction of the first plant material, and a thickness of the first plant material after compression is no more than 50% of a thickness of the first plant material prior to compression.

24. The method of claim 22, wherein the first density is in a range of 900-1200 kg/m^3, inclusive.

25. The method of claim 21, wherein 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.

26. The method of claim 25, wherein compressing is performed at a temperature in a range of 20-60 °C.

27. The method of claim 21, wherein compressing is performed such that the stabilizing agent and/or stabilizing agent precursors within the first plant material do not crosslink the amorphous cellulose and/or hemicellulose regions.

28. The method of claim 21, further comprising drying the first plant material to a moisture content in a range of 15-25 wt%, inclusive, after infiltrating the first plant material with the solution and prior to compressing the first plant material.

29. The method of claim 21, further comprising drying the first plant material to have a water content of 1-10 wt%, inclusive, after compressing the first plant material.

30. The method of claim 29, wherein the water content of the first plant material after drying is about 5 wt%.

31. The method of claim 29, further comprising further compressing the first plant material after drying the first plant material.

32. The method of claim 31, wherein the first plant material is further compressed to have a second density of at least 1200 kg/m^3.

33. The method of claim 31, wherein crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent occurs during further compressing the first plant material.

34. The method of claim 31, wherein crosslinking the amorphous cellulose and/or hemicellulose regions with the stabilizing agent occurs after further compressing the first plant material.

35. The method of claim 32, wherein the second density is in a range of 1200-1450 kg/m^3, inclusive.

36. The method of claim 31, wherein 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.

37. The method of claim 1, wherein, during infiltrating the first plant material with the solution:

(i) the stabilizing agent is hydrophilic and has a water solubility such that at least 30g thereof dissolves in 100 mL of water at 20 °C;

(ii) the stabilizing agent precursors are hydrophilic and have a water solubility such that at least 2g thereof dissolves in 100 mL of water at 20 °C; or

(iii) a combination of (i) and (ii).

38. The method of claim 1, wherein the amorphous cellulose and/or hemicellulose regions remain hydrophilic after being crosslinked.

39. The method of claim 1, wherein an amount of stabilizing agent and/or stabilizing agent precursors absorbed within the cell walls of the first plant material after infiltrating the first plant material with the solution is in a range of 1-25 wt%, inclusive, of the first plant material in a dry state prior to infiltrating.

40. The method of claim 1, wherein infiltrating the first plant material with the solution is performed at a temperature in a range of 20-50 °C, inclusive.

41. The method of claim 1, further comprising infiltrating an initial plant material with a loading solution prior to infiltrating the first plant material with the solution comprising the stabilizing agent and/or the stabilizing agent precursors.

42. The method of claim 41, wherein the loading solution and/or the solution comprising the stabilizing agent or the stabilizing agent precursors comprises water, sodium hydroxide, a catalyst, or any combination thereof.

43. The method of claim 1, wherein the nucleophile is phenol or cresol, and the electrophile is an oxazolidine or a bisoxazolidine.

44. The method of claim 1, wherein the first plant material is wood.

45. The method of claim 1, wherein the first plant material is bamboo.

46. A structure formed by the method of any one of claims 1-45.

47. A structure comprising:

a plant material having one or more cell walls comprising an amorphous cellulose region and a hemicellulose region; and

a stabilizing agent crosslinking the amorphous cellulose region and/or the hemicellulose region of the one or more cell walls of the plant material to form a crosslinked plant material,

wherein the stabilizing agent is a reaction product of a nucleophile and an electrophile, and

each of the nucleophile, the electrophile, and the stabilizing agent have a molecular weight less than or equal to 500 g/mole prior to crosslinking.

48. The structure of claim 47, wherein a level of swelling of the plant material, with the stabilizing agent therein, along a thickness direction of the plant material is no more than 10% regardless of a duration of exposure to water and/or an amount of water absorbed by the plant material.

49. The structure of claim 47, wherein:

the nucleophile comprises an aromatic nucleophile;

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

50. The structure of claim 49, wherein:

(i) the aromatic nucleophile comprises phenol or cresol;

(ii) the electrophile is soluble in water and comprises formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, or glutaraldehyde; or

(iii) a combination of (i) and (ii).

51. The structure of claim 47, nucleophile is phenol or cresol, and wherein the electrophile is an oxazolidine or a bisoxazolidine.

52. The structure of claim 47, wherein at least a portion of a lignin in the plant material is modified as compared to a lignin of a native plant material.

53. The structure of claim 52, 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.

54. The structure of claim 47, wherein a lignin content of the plant material is less than that in a native plant material.

55. The structure of claim 47, wherein the crosslinked plant material has a density of at least 900 kg/m^3.

56. The structure of claim 47, wherein the crosslinked plant material has a density of at least 1200 kg/m^3.

57. The structure of claim 47, wherein the crosslinked plant material has a density in a range of 1200-1450 kg/m^3, inclusive.

58. The structure of claim 47, wherein the plant material is a densified piece with native lumina formed by the one or more cell walls of the plant material that are substantially collapsed and cellulose-based fibers forming the cell walls being aligned along a common direction.

59. The structure of claim 47, wherein (i) the stabilizing agent is hydrophilic, and/or (ii) the amorphous cellulose region and/or the hemicellulose region that is crosslinked with the stabilizing agent is hydrophilic.

60. The structure of claim 47, wherein the stabilizing agent has a water solubility such that at least 2 g of the stabilizing agent dissolves in 100 mL of water at a temperature of 20 °C.

61. The structure of claim 47, wherein the stabilizing agent has a water solubility such that at least 30 g of the stabilizing agent dissolves in 100 mL of water at a temperature of 20 °C.

62. The structure of claim 47, wherein the plant material is wood.

63. The structure of claim 47, wherein the plant material is bamboo.

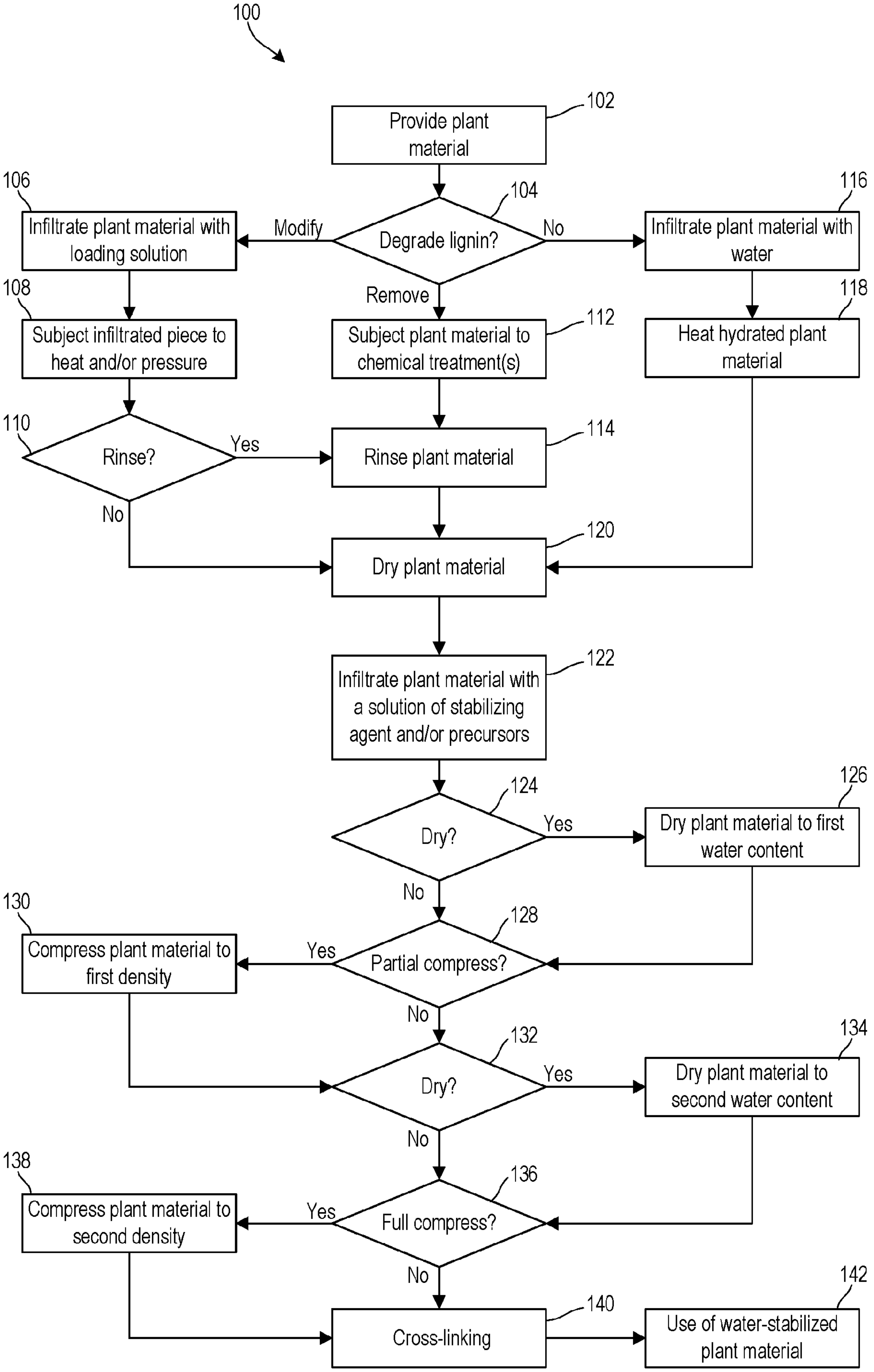
100
Provide plant material
102
Degrade lignin?
104
Modify
Infiltrate plant material with loading solution
106
No
Infiltrate plant material with water
116
Remove
Subject infiltrated piece to heat and/or pressure
108
Subject plant material to chemical treatment(s)
112
Heat hydrated plant material
118
Rinse?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

FIG. 1

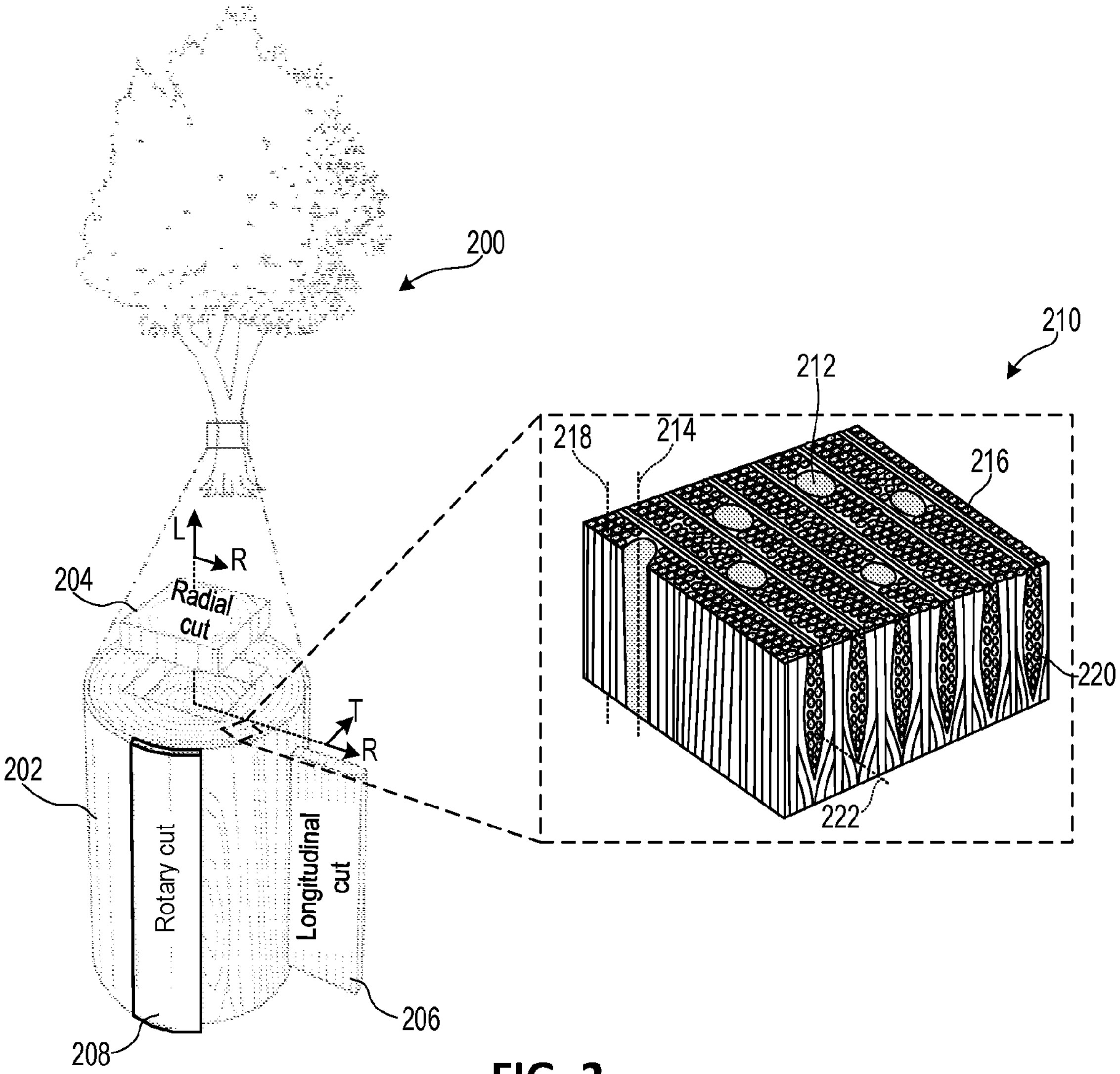
200
210
212
218
214
216
220
222
L
R
204
Radial cut
T
R
202
Rotary cut
Longitudinal cut
206
208

FIG. 2

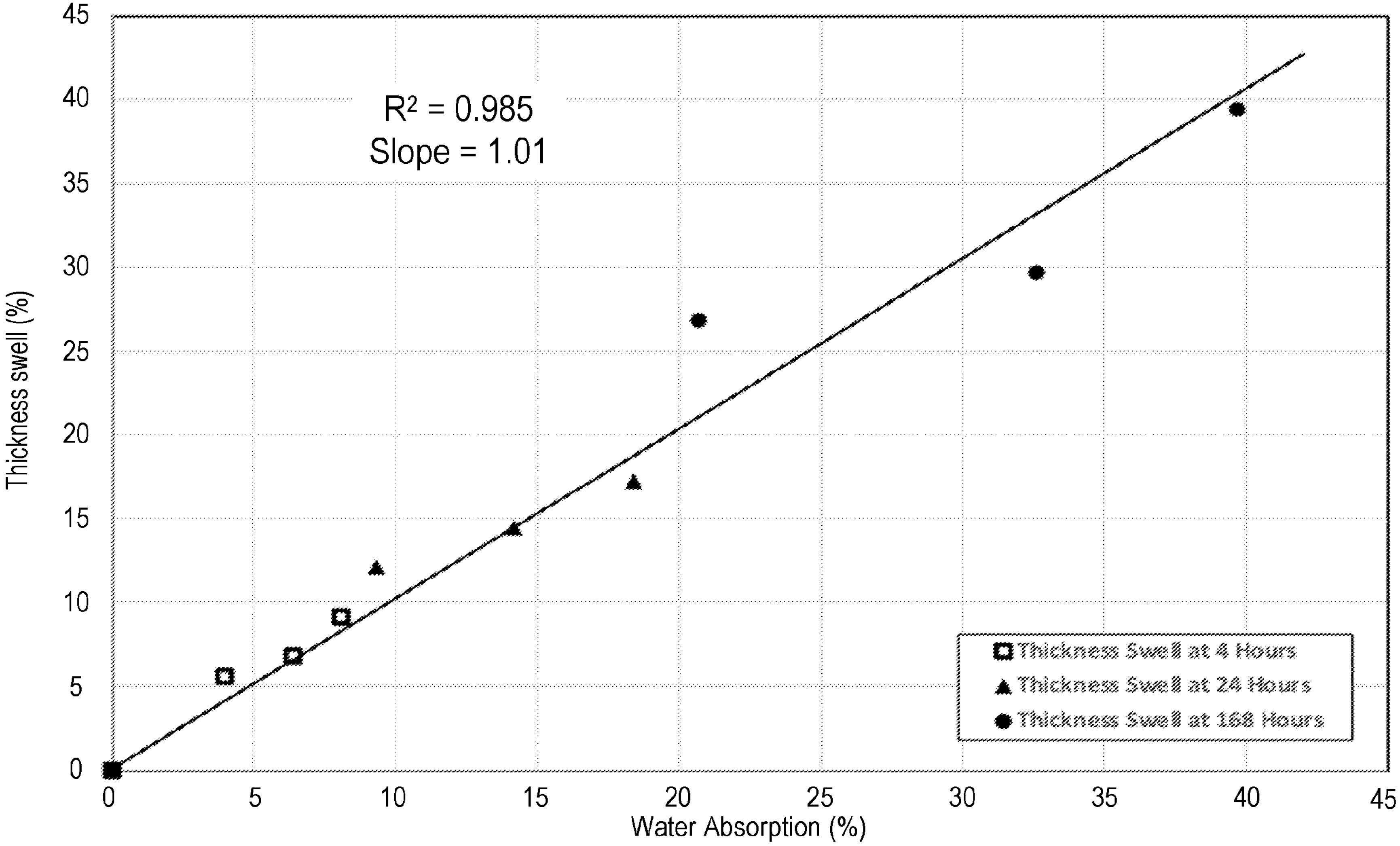
45
40
35
30
25
20
15
10
5
0
Thickness swell (%)
0
5
10
15
20
25
30
35
40
45
Water Absorption (%)
R² = 0.985
Slope = 1.01
□ Thickness Swell at 4 Hours
▲ Thickness Swell at 24 Hours
● Thickness Swell at 168 Hours

FIG. 3A

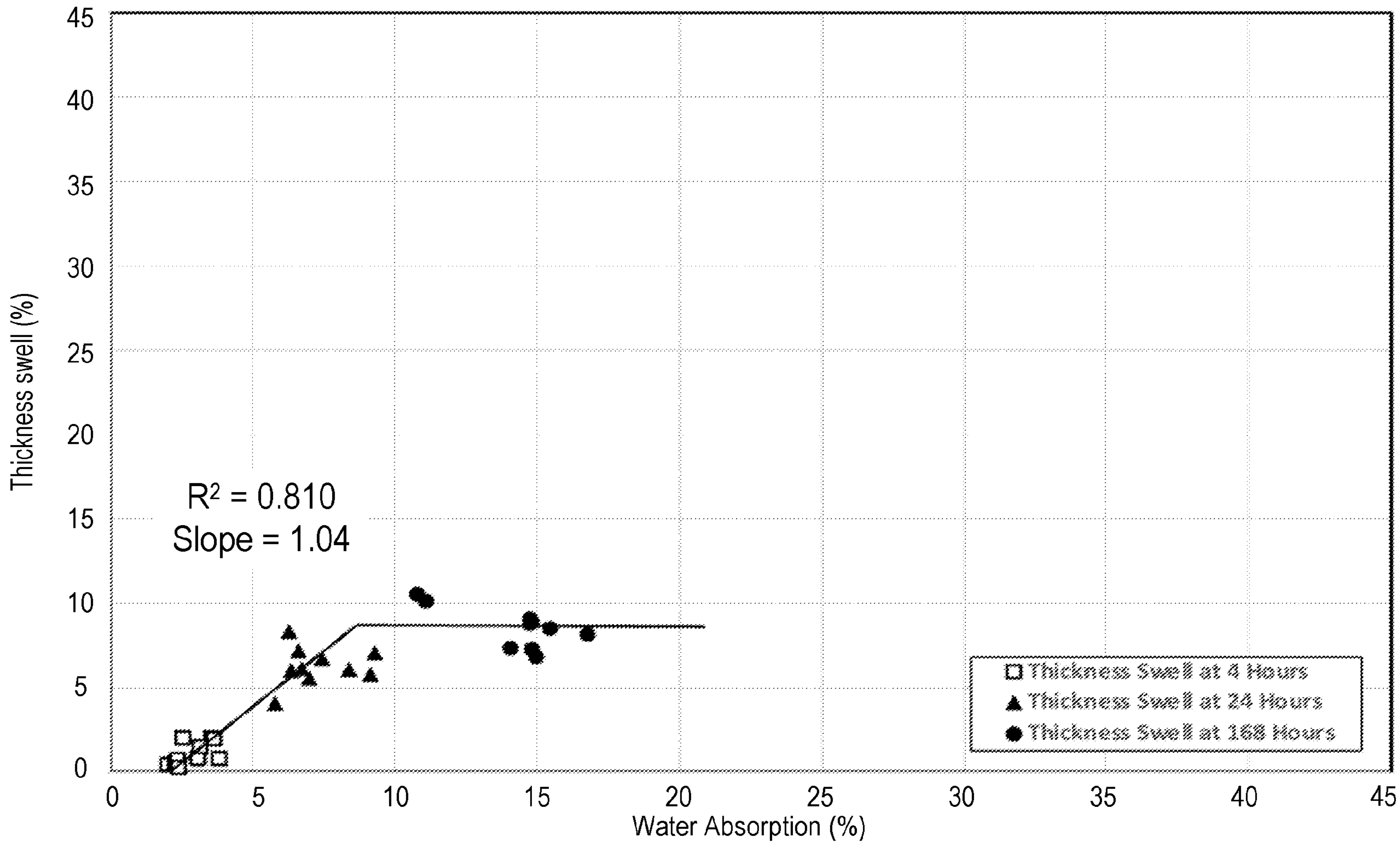
45
40
35
30
25
20
15
10
5
0
Thickness swell (%)
R² = 0.810
Slope = 1.04
0
5
10
15
20
25
30
35
40
45
Water Absorption (%)
☐ Thickness Swell at 4 Hours
▲ Thickness Swell at 24 Hours
● Thickness Swell at 168 Hours

FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/025554

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***B27K 3/15*** (2024.01); ***B27K 3/38*** (2024.01); ***B27K 3/50*** (2024.01); ***B27K 5/06*** (2024.01); ***B27K 9/00*** (2024.01); ***C08G 8/10*** (2024.01); ***C08J 3/24*** (2024.01); ***C08L 97/02*** (2024.01); ***B27K 3/02*** (2024.01); ***B27K 3/08*** (2024.01)

CPC: ***B27K 3/15; B27K 3/0207; B27K 3/083; B27K 3/38; B27K 3/50; B27K 5/06; B27K 9/002; C08G 8/10; C08J 3/24; C08L 97/02;*** *B27K 2240/10; B27K 2240/70*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WANG et al. Effect of Phenol Formaldehyde Resin Penetration on the Quasi-Static and Dynamic Mechanics of Wood Cell Walls Using Nanoindentation, Nanomaterials, Vol. 9, No. 10, 02 October 2019 [Retrieved on 04 June 2024]. Retrieved from the Internet: <URL: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6836151/>. entire document	1, 3-5, 7, 37, 40, 44
Y		6, 8-12, 15-18, 20-26, 28, 39, 41, 42, 45
Y	YUE et al. Use impregnation and densification to improve mechanical properties and combustion performance of Chinese fir, Construction and Building Materials, Vol. 241, 30 April 2020 [Retrieved on 26 June 2024]. Retrieved from the Internet: <URL: https://www.sciencedirect.com/science/article/abs/pii/S0950061820301069?via%3Dihub>. entire document	6, 21, 28

☑ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **27 June 2024 (27.06.2024)**	Date of mailing of the international search report **29 July 2024 (29.07.2024)**
Name and mailing address of the ISA/US **Mail Stop PCT, Attn: ISA/US** **Commissioner for Patents** **P.O. Box 1450, Alexandria, VA 22313-1450** Facsimile No. **571-273-8300**	Authorized officer **MATOS** **TAINA** Telephone No. **571-272-4300**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2022/0134596 A1 (BOITOUZET) 05 May 2022 (05.05.2022) entire document	8-12, 15-18, 20, 41, 42
Y	US 2020/0238565 A1 (UNIVERSITY OF MARYLAND COLLEGE PARK) 30 July 2020 (30.07.2020) entire document	21-26
Y	FURUNO et al. The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls, Wood Science and Technology, Vol. 37, 19 November 2003 [Retrieved on 27 June 2024]. Retrieved from the Internet: <URL: https://link.springer.com/article/10.1007/s00226-003-0176-6>. Pgs. 349-361	39
Y	US 2022/0412002 A1 (UNIVERSITY OF MARYLAND COLLEGE PARK) 29 December 2022 (29.12.2022) entire document	45
A	LANG et al. Influence of Phenol–Formaldehyde Resin Oligomer Molecular Weight on the Strength Properties of Beech Wood, Forests, Vol. 13, No. 12, 23 November 2022 [Retrieved on 27 June 2024]. Retrieved from the Internet: <URL: https://www.mdpi.com/1999-4907/13/12/1980>. entire document	1-45

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☑ Claims Nos.: **46**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-45 are drawn to methods.

Group II: claims 47-63 are drawn to structures.

The inventions listed in Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, methods, are not present in Group II; and the special technical features of Group II, structures, are not present in Group I.

Additionally, even if Groups I-II were considered to share the technical features of a plant material having one or more cell walls comprising an amorphous cellulose region and a hemicellulose region; and a stabilizing agent crosslinking the amorphous cellulose region and/or the hemicellulose region of the one or more cell walls of the plant material to form a crosslinked plant material, wherein the stabilizing agent is a reaction product of a nucleophile and an electrophile, and each of the nucleophile, the electrophile, and the stabilizing agent have a molecular weight less than or equal to 500 g/mole prior to crosslinking, these shared technical features do not represent a contribution over the prior art as disclosed by "Effect of Phenol Formaldehyde Resin Penetration on the Quasi-Static and Dynamic Mechanics of Wood Cell Walls Using Nanoindentation" to Wang et al. (hereinafter, "Wang").

Wang teaches a plant material having one or more cell walls (Abstract) comprising an amorphous cellulose region and a hemicellulose region (it is understood the cell walls of wood comprises an amorphous cellulose region and a hemicellulose region); and a stabilizing agent (pg 1 para 1 water-soluble PF has been widely applied as a modifier for improving the properties of wood, such as its strength, dimensional stability…) crosslinking the amorphous cellulose region and/or the hemicellulose region of the one or more cell walls of the plant material to form a crosslinked plant material (pg 8 para 2 The cross-linking between -OH groups of wood polymer with and resins may reinforce the cell wall; pg 7 para 1 the chemical reactions between -OH groups mainly existed in the amorphous region of the wood), wherein the stabilizing agent is a reaction product of a nucleophile and an electrophile (pg 2 para 4 Phenol formaldehyde (PF) resin; it is understood that this is a

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

product of nucleophile phenol and electrophile formaldehyde), and each of the nucleophile, the electrophile, and the stabilizing agent have a molecular weight less than or equal to 500 g/mole prior to crosslinking (pg 5 para 2 the molecular weight of most oligomers in the uncured PF resin was less than 500 Da; it is understood phenol has a molecular weight of about 94 g/mol and formaldehyde has a molecular weight of about 30 g/mol).

The inventions listed in Groups I-II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-45**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.