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(54) Title: ODOR IMPROVED SOY RESINS AND COMPOSITES

(57) Abstract: The present invention is a biodegradable composition comprising a resin containing soy protein and an essential oil, e.g. extract from the tea tree plant. Also included is a method of making the soy protein resin. The resin has improved properties for treating odor and for preventing microbial decay.



WO 2009/079583 A1

ODOR IMPROVED SOY RESINS AND COMPOSITES

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional 61/014,174 filed December 17,
5 2007, which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention, generally, relates to composites that are biodegradable and free of formaldehyde and more particularly to soy base composites.

BACKGROUND OF THE INVENTION

10 Urea-Formaldehyde (UF) resins are widely used as a binder for use in oriented strand board and particle board. These formaldehyde-based resins are inexpensive, colorless, and are able to cure fast to form a rigid polymer. Despite the effectiveness of the UF resins, particle board and oriented strand board often has a reputation for being of poor quality. Included in the quality is concern about the rate that these composites
15 degrade when exposed to water or heat and humidity.

Another serious disadvantage of UF resin-bonded wood products is that they slowly emit formaldehyde into the surrounding environment. Formaldehyde is part of a class of compounds that are commonly known as Volatile Organic Compounds (VOCs). Due to environmental, health, and regulatory issues related to formaldehyde emissions
20 from wood products, there is a continuing need for alternative formaldehyde-free binders. Recent legislation has prohibited or severely restricted the use of formaldehyde in furniture and building materials in one or more states.

A number of formaldehyde-free compositions have been developed for use as a binder for making wood products. U.S. Pat. No. 4,395,504 discloses the use of
25 formaldehyde-free adhesive system prepared by a reaction of a cyclic urea with glyoxal, for the manufacture of particleboard. Such a system, however, showed a rather slow cure and required acidic conditions (low pH) for the cure.

U.S. Pat. No. 5,059,488 shows an advantage of glutaraldehyde over glyoxal, when used in a reaction with cyclic urea. The patent discloses the use of glutaraldehyde-ethylene urea resins for wood panel manufacture. It was shown that this resin cured faster than glyoxal-ethylene urea resin, and the cure can be performed at a relatively high pH. However, the glutaraldehyde-based resins are not economically feasible.

U.S. Pat. No. 4,692,478 describes a formaldehyde-free binder for particleboard and plywood prepared of carbohydrate raw material such as whey, whey permeate, starch and sugars. The process comprises hydrolysis of the carbohydrate by a mineral acid, and then neutralizing the resin by ammonia. Although the raw materials are cheap and renewable, the reaction has to be performed at about 0.5. The pH makes handling difficult, dangerous, and costly.

U.S. Pat. No. 6,822,042 also discloses the use of a carbohydrate material (corn syrup) for preparing a non-expensive wood adhesive. Advantages of this binder include strong bonding, low cost, and renewable raw material. However, this adhesive requires the use of isocyanate as a cross-linker for this composition. Isocyanates are toxic making the use as a substitute for formaldehyde undesirable.

U.S. Pat. No. 6,599,455 describes a formaldehyde-free binder for producing particleboard containing curable thermoplastic co-polymers and cross-linkers selected from epoxy, isocyanate, N-methylol and ethylene carbonate compounds. Such compositions provide good strength and water resistance when cured. The epoxys are economically unfeasible do to the high material cost.

U.S. Pat. No. 6,348,530 describes a formaldehyde-free binder for producing shaped wood articles comprising a mixture of hydroxyalkylated polyamines and polycarboxylic acids. The binder preparation requires difficult steps to producte and as a result is not economically viable.

The state of the art is to find a resin that would be an effective replacement of formaldehyde resins. However, it would be desirable to provide a panel that exceeds the current state of the art of particle board in strength. It would be further advantageous if this material was biodegradable, substantially, if not entirely from renewable sources, was environmentally friendly, It would be further advantageous if

the panels having comparable strength to state of the art particle board was lighter weight, used less bulky materials, and had a lower profile. It is desirable that such curable compositions contain relatively high amount of non-volatiles, and at the same time are stable, fast-curing and do not emit any toxic fumes during the cure and afterwards. It would be desirable for the product to be not harmful to the environment when placed in a landfill.

Soy protien resins such as those disclosed in U.S. Publication No. 2006/0264135 provide composites that have promising applications as a replacemnt for oriented strand board that have many if not all of the desirable characteristics relating to environmentally friendly materials. However, soy protien compositions have been known to emit an odor that is pungent and considered undesirable. Many efforts have been made in the food procesing arena to reduce the malodorous properties of soy protien. However, many such applications have questionable applicability to soy protein resins for building materials, panels and furniture.

U.S. Patent No. 7,169,425 uses size exclusion chromatography to remove smaller molecular weight particles that are responsible for the taste and odor of soy protein. However, such a process may not be feasible or economical for large scale use in manufacturing composites that are used in furniture manufacturing, building materials, panels etc.

U.S. Patent No. 7147878 requires the addition of compounds with disulfide bonds including certain peptides. Presently, it is unknown whether the compounds disclosed in this patent would be useful for furniture that is heat pressed under the extreme conditions required to make the soy composites. Thus, it would be desirable if there was a deodorant that could control the odor of soy in an economically feasible way for manufacturing furniture. It is further desirable for the treatment to be effective after conditions of heat pressing. Moreover, it would be desirable if the deodorant had antimicrobial properties and slowed the breakdown of product under conditions of normal use. The present invention addresses one or more of these and other needs.

SUMMARY OF THE INVENTION

The present invention includes a biodegradable composition comprising a resin containing soy protein and an essential oil, e.g. an extract from the melaleuca plant.

In one embodiment, the present invention is a method for preparing a biodegradable composite sheet comprising a step of preparing a resin comprising soy protein and an essential oil, e.g. an extract from the melaleuca plant. A fiber mat is impregnated with said resin. Water is removed to form a precured sheet. The precured sheet is subjected to conditions of temperature and pressure effective to form a biodegradable composite sheet.

In one embodiment, the essential oil is present in an amount that is a minimum of about 0.05% and a maximum of about 2% based upon the dry weight of the resin.

In another embodiment, the composition includes a carboxy-containing polysaccharide.

In still another embodiment, the carboxy-containing polymer is selected from the group consisting of agar, gellan, and mixtures thereof.

In one embodiment, the resin further comprises nanoclay.

In still another embodiment, the resin further comprises nanofibers and microfibers, wherein the nanofibers and microfibers are biodegradable.

In still another embodiment, the composition includes nanofibers and microfibers comprising microfibrillated cellulose and nanofibrillated cellulose.

In an embodiment, the resin is impregnated into mats of fibers selected from the group consisting of hemp, kenaf, sorghum, jute, flax, sisal, banana, kapok, bamboo, ramie, pineapple and combinations thereof.

In one embodiment, the mats are made of a reinforcing fiber, a reinforcing filament, a reinforcing yarn, a woven fabric, a knitted fabric, a non-woven fabric, and combinations thereof.

In still another embodiment, the composition further comprises a plasticizer. Typically, the plasticizer is comprises one or more of glycerol, propylene glycol,

polyethylene glycol, manitol, xylitol, sorbitol or other polyols. Plasticizers of one embodiment include fatty acids or oils. Preferably, plasticizers are biodegradable, from a renewable source and are non-toxic.

Preferably, in an embodiment, the composition is substantially free of starch.

- 5 Alternatively or additionally, the composition is substantially free of cross-linking agent.

In one embodiment the composition is mad at a temperature and pressure effective for preparing a biodegradable composite sheet comprise a temperature of about 80°C to about 120°C and a pressure of about 3 MPa to about 20 MPa.

10 **DETAILED DESCRIPTION OF THE INVENTION**

Definitions

- The term "biodegradable" is used herein to mean degradable over time by water, microbes and/or enzymes found in nature (e.g. compost), without harming the environment. To be considered strictly biodegradable a material is required to degrade
15 a minimum of 60% within 180 days under compostable conditions that are defined by ASTM D790.

The terms "biodegradable resin" and "biodegradable composite" are used herein to mean that the resin and composite are sustainable and at the end of their useful life, can be disposed of or composted without harming, in fact, helping the environment.

- 20 The term "stress at maximum load" means the stress at load just prior to fracture, as determined by the stress-strain curve in a tensile test.

The term "fracture stress" means the stress at fracture as determined by the stress-strain curve in a tensile test.

- The term "fracture strain" means the strain (displacement) at fracture, as determined
25 by the stress-strain curve in a tensile test.

The term "modulus" means stiffness, as determined by the initial slope of the stress-strain curve in a tensile test.

The term "toughness" means the amount of energy used in fracturing the material, as determined by the area under the stress-strain curve.

The "tensile test" referred to is carried out using Instron or similar testing device according to the procedure of ASTM Test No. D882 for resin sheets and D3039 for
5 composites. Testing is carried out after 3 days conditioning at 21°C and 65% R.H.

The term "strengthening agent" is used herein to describe a material whose inclusion in the biodegradable polymeric composition of the present invention results in an improvement in any of the characteristics "stress at maximum load", "fracture stress", "fracture strain", "modulus", and "toughness" measured for a solid article formed by
10 curing of the composition, compared with the corresponding characteristic measured for a cured solid article obtained from a similar composition lacking the strengthening agent.

The term "curing" is used herein to describe subjecting the composition of the present invention to conditions of temperature and effective to form a solid article having a
15 moisture content of preferably less than about 0.5 wt. %.

The phrase "free of formaldehyde" or "formaldehyde free" means the materials used do not contain formaldehyde or a compound that will release formaldehyde in the manufacturing process or during the effective life of the product.

Resin

20 The present invention includes an oil of the melaleuca plant. Also referred to as tea tree oil, when added to soy resin it imparts two key quality improvements that result in a surprising benefit. The soy odor is controlled or at least improved. Furthermore, the tea tree oil has antimicrobial properties that will extend the life of the board during its useful life.

25 The tea tree oil is available from a wide number of sources on the internet including Australian Botanical Products Pty, Ltd, from Victoria, Australia. Tea tree oil is an essential oil that is, in one embodiment, steam distilled from the Australian plant *Melaleuca alternifolia*. It has also been known as melaleuca oil. Tea tree oil contains over 100 components, mostly monoterpenes, sesquiterpenes and their alcohols. The

component terpinen-4-ol is the most abundant (minimum 30%) and is said to be responsible for most of the antimicrobial activity. Tea tree oil is a general antimicrobial agent with effectiveness against gram positive bacteria, gram negative bacteria and fungus.

- 5 The gram positive bacteria that tea tree oil is effective against includes but is not limited to *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Staphylococcus pneumoniae*, *Staphylococcus faecalis*, *Staphylococcus pyrogenes*, *Staphylococcus agalactiae*, *Propionibacterium acnes*, and *Betahaemolytic streptococcus*. The gram negative bacteria that tea tree oil is effective against includes but is not limited to *Escherichia coli*,
- 10 *Klebsiella pneumoniae*, *Citrobacter* ssp, *Shigella sonnei*, *Proteus mirabilis*, *Legionella* ssp, and *Pseudomonas aeruginosa*. The fungi that tea tree oil is effective against are *Trichophyton mentagrophytes*, *Trichophyton rubrum*, *Aspergillus niger*, *Aspergillus flavus*, *Candida albicans*, *Microsporum canis*, *Microsporum gypseum*, and *Thermoactinomyces vulgaris*.
- 15 Thus, in one embodiment, the present invention includes a resin comprising monoterpenes and sesquiterpenes and soy protein. In another embodiment, the present invention includes terpinen-4-ol in combination with soy protein. In another embodiment, the present invention includes a resin comprising essential oils in combination with soy protein. Essential oils are defined as both oily or non-oily,
- 20 volatile aromatic substance constituting the chemical principal of the plant. Essential oils are typically extracted by distillation or expression. Essential oils often possess antibiotic, antiviral, anti-fungal and other antimicrobial properties. Essential oils are typically able to penetrate cell structures to affect the desired antimicrobial result. Essential oils are often used topically in pure form or diluted in carrier oil. Essential
- 25 oils are often known to contain vitamins, hormones, antibiotics, and/or antiseptics.

In one embodiment, the essential oil includes one or more of the following: agar oil, ajwain oil, angelica root oil, anise oil, balsam oil, basil oil, buchu oil, bergamot oil, black pepper oil, cannabis flower essential oil, caraway oil, cardamom seed oil, carrot seed oil, cedarwood oil, chamomile oil, cinnamon oil, cistus oil, citronella oil, clary sage; clove leaf oil, coriander oil, costmary oil, cranberry seed oil, cumin oil (black seed oil), cypress oil, davana oil, dill oil, eucalyptus oil, fennel seed oil, fenugreek oil, fir oil, frankincense oil, galbanum, geranium oil, ginger oil, goldenrod, grapefruit oil,

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henna oil, helichrysum, hyssop, idaho tansy, jasmine oil, juniper berry oil, lavender oil, ledum, lemon oil, lemongrass, litsea cubeba oil, marjoram, melaleuca oil (tea tree oil), melissa oil (lemon balm), mentha arvensis oil (mint oil), mountain savory, mustard oil, myrrh oil, myrtle, neroli, nutmeg, orange oil, oregano oil, orris oil, palo santo, parsley oil, patchouli oil, perilla, peppermint oil, petitgrain, pine oil, ravensara, red cedar, roman chamomile, rose oil, rosehip oil, rosemary oil, rosewood oil, sage oil, sandalwood oil, sassafras oil, savory oil, schisandra oil, spearmint oil, spikenard, spruce, star anise oil, tangerine, tarragon oil, thyme oil, tsuga, valerian, vetiver oil, western red cedar, wintergreen, yarrow oil, and ylang-ylang. In a preferred embodiment, the essential oil is one or more from the group including davana oil, eucalyptus oil, lemon oil, lemongrass, orange oil, oregano oil, pine oil, rosemary oil, and melaleuca oil (tea tree oil).

The essential oil, including tea tree oil, is added to the resin prior to impregnation and thoroughly mixed. The amount of essential oil (including tea tree oil) as a weight percent of the solid components of the resin is a minimum of about 0.05%, about 0.1 wt. %, about 0.2 wt. %, about 0.4 wt. %, about 0.5 wt. % and/or a maximum of about 2%, about 1.5 wt. %, about 1 wt. %, about 0.8 wt. %, about 0.5 wt. % based upon the dry weight of the resin.

In one embodiment, the resin includes soy protein and a soluble strengthening agent (i.e., substantially soluble in water at a pH of about 7.0 or higher. In one embodiment, the soluble strengthening agent is a polysaccharide. Preferably, the polysaccharide is a carboxy-containing polysaccharide. In one preferred embodiment, the soluble strengthening agent is selected from the group consisting of agar, gellan, and mixtures thereof.

Soy protein is the basis for the resin of the present invention, soy protein can be obtained in soy flour, soy protein concentrate and soy protein isolate. Each of these sources has increasing concentrations of soy protein. Preferably, soy protein concentrate is used because of it has an excellent tradeoff between cost and concentration of soy protein.

The amount of soy protein added to the fiber mats, fabrics or yarns results in composite panels that have a minimum of about 30 wt. % soy protein, about 35 wt. %

soy protein, about 40 wt. % soy protein, about 50 wt. % soy protein and/or a maximum of about 70 wt. % soy protein, about 65 wt. % soy protein, about 60 wt. % soy protein, about 55 wt. % soy protein or about 50 wt. % soy protein based upon the final weight of the finished panel.

- 5 Soy protein has been modified in various ways and used as resin in the past, as described in, for example, Netravali, A.N. and Chabba, S., *Materials Today*, pp. 22-29, April 2003; Lodha, P. and Netravali, A.N., *Indus. Crops and Prod.* 2005, 21, 49; Chabba, S. and Netravali, A.N., *J. Mater. Sci.* 2005, 40, 6263; Chabba, S. and Netravali, A.N., *J. Mater. Sci.* 2005, 40, 6275; and Huang, X. and Netravali, A.N.,
- 10 *Biomacromolecules*, 2006, 7, 2783.

- Soy protein contains about 20 different amino acids, including those that contain reactive groups such as -COOH, -NH₂ and -OH groups. Once processed, soy protein itself can form crosslinks through the -SH groups present in the cysteine amino acid as well as through the dehydroalanine (DHA) residues formed from alanine by the
- 15 loss of side chain beyond the β -carbon atom. DHA is capable of reacting with lysine and cysteine by forming lysinoalanine and lanthionine crosslinks, respectively. Asparagines and lysine can also react together to form amide type linkages. All these reactions can occur at higher temperatures and under pressure that is employed during curing of the soy protein.

- 20 In addition to the self-crosslinking in soy protein, the reactive groups can be utilized to modify soy proteins further to obtain desired mechanical and physical properties. The most common soy protein modifications include: addition of crosslinking agents and internal plasticizers, blending with other resins, and forming interpenetrating networks (IPN) with other crosslinked systems. Without being limited to a particular
- 25 mechanism of action, these modifications are believed to improve the mechanical and physical properties of the soy resin.

- The properties (mechanical and thermal) of the soy resins can be further improved by adding nanoclay particles and micro- and nano-fibrillar cellulose (MFC, NFC), as described in, for example, Huang, X. and Netravali, A.N., "Characterization of flax
- 30 yarn and flax fabric reinforced nano-clay modified soy protein resin composites," *Compos. Sci. and Technol.*, in press, 2007; and Netravali, A.N.; Huang, X.; and

Mizuta, K., "Advanced green Composites," *Advanced Composite Materials*, submitted, 2007.

The resin can include additional non-soluble strengthening agents of natural origin that can be a particulate material, a fiber, or combinations thereof. The non-soluble strengthening agent may be, for example, a liquid crystalline (LC) cellulose nanoclay, microfibrillated cellulose, nanofibrillated cellulose.

Further in accordance with the present invention, a composition containing agar, agar agar or gellan and soy protein can be optionally employed together with natural and high strength liquid crystalline (LC) cellulosic fibers to form biodegradable composites. The LC cellulose fibers can be produced by dissolving cellulose in highly concentrated phosphoric acid to form a LC solution of cellulose, as described in Borstoel, H., "Liquid crystalline solutions of cellulose in phosphoric acid," Ph. D. Thesis, Rijksuniversiteit, Groningen, Netherlands, (1998). The resulting LC solution was spun using an air gap-wet spinning technique to obtain highly oriented and crystalline cellulose fibers that had strengths in the range of 1700 MPa.

The resin can include additional non-soluble strengthening agents of natural origin that can be a particulate material, a fiber, or combinations thereof. The non-soluble strengthening agent may be, for example, a liquid crystalline (LC) cellulose nanoclay, microfibrillated cellulose, nanofibrillated cellulose.

Gellan, a linear tetrasaccharide that contains glucuronic acid, glucose and rhamnose units, is known to form gels through ionic crosslinks at its glucuronic acid sites, using divalent cations naturally present in most plant tissue and culture media. In the absence of divalent cations, higher concentration of gellan is also known to form strong gels via hydrogen bonding. The mixing of gellan with soy protein isolate has been shown to result in improved mechanical properties. See, for example, Huang, X. and Netravali, A.N., *Biomacromolecules*, 2006, 7, 2783 and Lodha, P. and Netravali, A.N., *Polymer Composites*, 2005, 26, 647.

Gellan gum is commercially available as PhytigelTM from Sigma-Aldrich Biotechnology. It is produced by bacterial fermentation and is composed of glucuronic acid, rhamnose and glucose, and is commonly used as a gelling agent for

electrophoresis. Based on its chemistry, cured Phytigel™ is fully degradable. In preparing a composition of the present invention wherein cured gellan gum is the sole strengthening agent, Phytigel™ is dissolved in water to form a solution or weak gel, depending on the concentration. The resulting solution or gel is added to the initial
5 soy protein powder suspension, with or without a plasticizer such as glycerol, under conditions effective to cause dissolution of all ingredients and produce a homogeneous composition.

Preferably, the weight ratio of soy protein:strengthening agent in the resin of the present invention is a minimum of about 20:1, about 15:1, about 10:1, about 8:1,
10 about 4:1, about 3:1 and/or a maximum of about 1:1, about 2:1, about 2.5:1, about 3:1 and about 4:1.

In still another embodiment, the composition further comprises a plasticizer. Typically, the plasticizer is comprises one or more of glycerol, propylene glycol, polyethylene glycol, manitol, xylitol, sorbitol or other polyols. Plasticizers of one
15 embodiment include fatty acids or oils. Preferably, plasticizers are biodegradable, from a renewable source and are non-toxic.

The weight percentage of plasticizer in the resin (excluding water) is a minimum of about 5 wt.%, about 8 wt.%, about 10 wt.%, about 12 wt.% or about 15 wt.% and/or a maximum of about 20 wt.%, about 18 wt.%, about 15 wt.%, about 12 wt.% or about
20 10 wt.%.

The biodegradable polymeric composition of the present invention preferably is substantially free of a starch additive. The biodegradable polymeric composition is substantially free of supplementary crosslinking agents such as, for example, acid anhydrides, isocyanates and epoxy compounds.

25 The Fiber Mats

In accordance with the present invention, the soy impregnated fiber mat plies are made of biodegradable fiber mats and biodegradable polymeric resin that comprises soy protein. Preferably the mats are biodegradable and are from a renewable natural resource.

In one embodiment, the fabrics are any biodegradable material that has fibers useful in making fabric, cords or string. In one embodiment, the biodegradable fibers are made of cotton, silk, spider silk, hemp, ramie, kenaf, sorghum, burlap, flax, sisal, kapok, banana, pineapple wool, hair or fur, jute, polylactic acid (PLA), viscose rayon, lyocell, or combinations thereof.

In one embodiment, the fabrics are preferably hemp, ramie, kenaf, sorghum, burlap, flax, sisal, kapok, banana or pineapple fibers.

In an embodiment, the fibers are yarn, woven, nonwoven, knitted or braided. The mats are preferably of uniform thickness and water absorbent to facilitate easy impregnation of the mats by soy fiber. In one embodiment, the mats are nonwoven and have a mass per area that is a minimum of about 100 g/m^2 , about 200 g/m^2 or about 300 g/m^2 and/or a maximum of about 500 g/m^2 , about 600 g/m^2 or about 800 g/m^2 .

In one preferred embodiment, the mats are nonwoven and are made of natural fibers (e.g. kenaf fibers) that are blended with polylactic acid and heat pressed into a nonwoven fiber mat of uniform thickness. The polylactic acid readily melts during the heat press stage and binds the kenaf fibers together. Other degradable fibers, e.g. wool, viscose rayon, lyocell, etc., may also be used.

Method of Making Resin

A biodegradable resin in accordance with the present invention may be prepared by the following illustrative procedure:

Into a mixing vessel at a temperature of about $70\text{--}85^\circ\text{C}$ is added 50-150 parts water, 1-5 parts glycerol, 10 parts soy protein concentrate or isolate, and 1-3 parts gellan or agar. Then from 0.05 wt.% to about 2 wt.% of tea tree oil based upon the dry weight of the resin is added to the mixture. Then, with vigorous stirring, a sufficient amount of aqueous sodium hydroxide is added to bring the pH of the mixture to about 11. The resulting mixture is stirred for 10-30 minutes, then filtered to remove any residual particles. Optionally, clay nanoparticles and/or cellulose nanofibers may be added to the resin solution as additional strengthening agents.

The Fiber Mats

In accordance with the present invention, the soy impregnated fiber mat plies are made of biodegradable fiber mats and biodegradable polymeric resin that comprises soy protein. Preferably the mats are biodegradable and from a renewable natural
5 resource.

In one embodiment, the fabrics are any biodegradable material that has fibers useful in making fabric, cords or string. In one embodiment, the biodegradable fibers are made of cotton, silk, spider silk, hemp, ramie, kenaf, sorghum, burlap, flax, sisal, kapok, banana, pineapple wool, hair or fur, jute, polylactic acid (PLA) , viscose rayon,
10 lyocell, or combinations thereof.

In one embodiment, the fabrics are preferably hemp, ramie, kenaf, sorghum, burlap, jute, flax, sisal, kapok, banana or pineapple fibers.

In an embodiment, the fibers are yarn, woven, nonwoven, knitted or braided. The mats are preferably of uniform thickness and water absorbent to facilitate easy
15 impregnation of the mats by soy based resin. In one embodiment the mats are nonwoven and have a mass per area that is a minimum of about 100 g/m^2 , about 200 g/m^2 or about 300 g/m^2 and/or a maximum of about 500 g/m^2 , about 600 g/m^2 or about 800 g/m^2 .

In one preferred embodiment, the mats are nonwoven and are made of natural fibers
20 (e.g. kenaf fibers) that are blended with a binding fiber that will bind to the natural fibers under conditions of heat and pressure. One example of a binding fiber is poly(lactic acid). Poly(lactic acid) fibers are blended with the natural fibers. The blended fibers are heat pressed. The poly(lactic acid) readily melts during the heat press stage and binds the kenaf fibers together. Degradable fibers that are capable of
25 binding to natural fibers to form a workable mat include wool, viscose rayon, lyocell, and poly(lactic acid) and combinations thereof.

In one embodiment, the non-woven mats comprise, prior to impregnation, a binding fiber in an amount that is a minimum of about 1 wt.%, about 2 wt.%, about 5 wt.%, about 7 wt.% and a maximum of about 20 wt.%, about 17 wt.%, about 15 wt.%, about

12 wt.% or about 10 wt.%. Optionally, the non-woven mats comprise, prior to impregnation, natural fiber that is a minimum of about 80 wt.%, about 82 wt.%, about 85 wt.%, about 87 wt.% or about 90 wt.%.

Method of Making Impregnated Fiber Mats

- 5 The resin solution so produced is used to impregnate and coat one or more fiber mats or fabric sheets. The mats may comprise, for example, burlap, flax, ramie, sisal, kapok, banana, pineapple, kenaf, hemp fiber or combinations thereof. In one embodiment, the fabric sheet is preferably flax. The mat is preferably jute or kenaf

- 10 Resin solution is applied to a fiber mat or sheet in an amount of about 50-100 ml of resin solution per 15 grams of fiber so as to thoroughly impregnate the mat or sheet and coat its surfaces. The mat or sheet so treated is pre-cured by drying in an oven at a temperature of about 35-70°C to form what is referred to as a prepreg.

- 15 The prepreg mats are arranged into sheets of sufficient size and are layered on top of one another. Care is taken to prevent any folding of the sheets which is often difficult to do when manufacturing sheets of considerable size. The prepreg sheets are sized to exceed recommended dimension by a minimum of 1 cm in length and width of the desired. Through experience it has been found that manufacture of a composite board of uniform thickness of a size greater than about 4 feet in length and two feet in width requires assembling pieces that are oversized. Otherwise, the edges of the board
20 cannot be made with uniform thickness desirable in a building product.

In one embodiment, a minimum of two prepreg sheets are stacked and aligned. In another embodiment, there are 4, 5, 6, 7, 8, 9, or 10 prepreg sheets.

- 25 Five sheets are stacked as described above and are subject to high pressure and temperature to cure. By way of example, the stack is hot pressed for 2-10 minutes at about 80°C and a load of 0.5-1 MPa. Following a rest period of about 5 minutes, the stack is hot pressed for 5-15 minutes at 120-130°C and a load of 2-10 MPa, followed by removal from the press. The resulting solid article has the appearance of a solid piece of material and a thickness of about 0.1 – 0.5 inches.

Then, the outer perimeter is cut to the desired size. The article is of uniform thickness and exhibits excellent strength properties.

The layers of material are stacked from one side to the other as follows:

NWM/WF/NWM/WF/NWM,

5 where NWM is non-woven mat, WF is a woven fabric.

A biodegradable composite article of the present invention may comprise a thermoset composite sheet in the form of a flat sheet, as just described. Alternatively, the thermoset sheet may be corrugated, with a lateral profile comprising alternating ridges and valleys.

10 The corrugated sheet may be formed using a conventional thermoforming molding process, using apparatus described in U.S. patents classified in class 425, subclasses 369 (apparatus wherein reshaping means creates accordion-like pleats or wrinkles or the like in a preform by distorting a section thereof transverse to its axis into a plurality of reversing curves) and 336 (apparatus comprising means for shaping an
15 advancing length of work into ridges and grooves).

Also envisioned in accordance with the present invention are biodegradable composite solid articles that comprise a stacked array of biodegradable composite sheets containing both flat and corrugated sheets. For example, the array could include a middle corrugated sheet disposed between and adhered to two flat sheets,
20 providing bending stiffness in the direction of the corrugations. In another configuration, two superimposed corrugated sheets whose corrugations are orthogonal to one another are secured between two flat outer sheets, resulting in a structure of enhanced stiffness in both directions.

Also in accordance with the present invention, a biodegradable molded thermoset
25 polymeric article is obtained by subjecting the biodegradable polymeric composition described above to conditions of temperature and pressure effective to form the thermoset polymeric article. Effective temperature and pressure conditions preferably comprise a temperature of about 35°C to about 130°C and a pressure of about 0.1

MPa to about 20 MPa, more preferably, a temperature of about 80°C to about 120°C and a pressure of about 4 MPa to about 20 MPa.

In one preferred embodiment, the molded thermoset polymeric article comprises a thermoset sheet, which may be included in a stacked array of thermoset sheets.

- 5 Alternatively, the biodegradable press-shaped thermoset polymeric article may be shaped by a mold.

Preferably, the biodegradable press-shaped thermoset polymeric article is characterized by a stress at maximum load of at least about 20 MPa and/or a modulus of at least about 300 MPa.

- 10 In one embodiment, the panels are of a size that is about 8 feet by four feet, four feet by two feet, and twelve feet by four feet. These panels have excellent nail and screw retention properties, can be painted effectively and are strong. They can be cut or drilled without frayed edges and are consistent in width throughout the surface area. In another embodiment, the panels are effective in making office cubicles and
- 15 partitions. In another embodiment, they are used for making cabinetry. In another embodiment, the panels are excellent for use in manufacturing furniture, particularly low profile furniture. Other applications include chairs, shelves, desks, tables and doors.

- In one embodiment of the present invention, one or two surfaces of the corrugated
- 20 board are laminated with a veneer. The veneer can improve appearance as well as water resistant properties of the corrugated board. The veneer of one embodiment is a wood veneer, or printed paper veneer. The veneer may be laminated or coated to produce a waterproof finish. The coating of one preferred embodiment incorporates a natural whey ingredient to improve its earth friendly properties according to formulas
- 25 known in the art. In another embodiment, the coating is not a biodegradable coating. For example polyurethane or epoxide coatings are used to cover the surface of the corrugated board. In another embodiment, formica is the laminated outer layer. While it is understood that non-biodegradable materials are less desirable from an ecological standpoint, the use of petroleum products on the outer layers is often
- 30 worthwhile for furniture or other objects to produce a long-lasting durable product where the bulk of that product is made from renewable and biodegradable materials.

While the invention has been described by reference to various specific embodiments, it should be understood that numerous changes may be made within the spirit and scope of the inventive concepts described. Accordingly, it should be recognized that the invention is not limited to the described embodiments.

CLAIMS

What is claimed is:

1. A biodegradable composition comprising a resin containing soy protein and essential oil.
2. The biodegradable composition of claim 1, wherein the essential oil is one or more oil selected from the group including agar oil, ajwain oil, angelica root oil, anise oil, balsam oil, basil oil, buchu oil, bergamot oil, black pepper oil, cannabis flower essential oil, caraway oil, cardamom seed oil, carrot seed oil, cedarwood oil, chamomile oil, cinnamon oil, cistus oil, citronella oil, clary sage, clove leaf oil, coriander oil, costmary oil, cranberry seed oil, cumin oil (black seed oil), cypress oil, davana oil, dill oil, eucalyptus oil, fennel seed oil, fenugreek oil, fir oil, frankincense oil, galbanum, geranium oil, ginger oil, goldenrod, grapefruit oil, henna oil, helichrysum, hyssop, idaho tansy, jasmine oil, juniper berry oil, lavender oil, ledum, lemon oil, lemongrass, litsea cubeba oil, marjoram, melaleuca oil (tea tree oil), melissa oil (lemon balm), mentha arvensis oil (mint oil), mountain savory, mustard oil, myrrh oil, myrtle, neroli, nutmeg, orange oil, oregano oil, orris oil, palo santo, parsley oil, patchouli oil, perilla, peppermint oil, petitgrain, pine oil, ravensara, red cedar, roman chamomile, rose oil, roschip oil, rosemary oil, rosewood oil, sage oil, sandalwood oil, sassafras oil, savory oil, schisandra oil, spearmint oil, spikenard, spruce, star anise oil, tangerine, tarragon oil, thyme oil, tsuga, valerian, vetiver oil, western red cedar, wintergreen, yarrow oil, and ylang-ylang.
3. A biodegradable composition comprising a resin containing soy protein and terpinen-4-ol.
4. A biodegradable composition comprising a resin containing soy protein and an extract from the melaleuca plant.
5. The composition of claim 4, wherein the oil is present in an amount that is a minimum of about 0.05% and a maximum of about 2% based upon the dry weight of the resin.

6. The composition of claim 4 further comprising mats of fibers selected from the group consisting of hemp, kenaf, sorghum, jute, flax, sisal, banana, kapok, bamboo, ramie, pineapple and combinations thereof, wherein the mats are impregnated with resin.

7. A method for preparing a biodegradable composite sheet comprising the steps of:

preparing a resin comprising soy protein and an essential oil;

coating and impregnating a fiber mat with said resin;

removing water, thereby forming a precured sheet; and

subjecting said precured sheet to conditions of temperature and pressure effective to form a biodegradable composite sheet.

8. The method of claim 7, wherein the essential oil is present in an amount that is a minimum of about 0.05% and a maximum of about 2% based upon the dry weight of the resin.

9. A biodegradable composite comprising a resin containing soy protein and essential oil impregnated in a biodegradable fiber sheet.

10. The biodegradable composite of claim 9, wherein the essential oil is one or more oil selected from the group including agar oil, ajwain oil, angelica root oil, anise oil, balsam oil, basil oil, buchu oil, bergamot oil, black pepper oil, cannabis flower essential oil, caraway oil, cardamom seed oil, carrot seed oil, cedarwood oil, chamomile oil, cinnamon oil, cistus oil, citronella oil, clary sage, clove leaf oil, coriander oil, costmary oil, cranberry seed oil, cumin oil, cypress oil, davana oil, dill oil, eucalyptus oil, fennel seed oil, fenugreek oil, fir oil, frankincense oil, galbanum, geranium oil, ginger oil, goldenrod, grapefruit oil, henna oil, helichrysum, hyssop, idaho tansy, jasmine oil, juniper berry oil, lavender oil, ledum, lemon oil, lemongrass, litsea cubeba oil, marjoram, melaleuca oil, melissa oil, mentha arvensis oil, mountain savory, mustard oil, myrrh oil, myrtle, neroli, nutmeg, orange oil, oregano oil, orris oil, palo santo, parsley oil, patchouli oil, perilla, peppermint oil, petitgrain, pine oil,

ravensara, red cedar, roman chamomile, rose oil, rosehip oil, rosemary oil, rosewood oil, sage oil, sandalwood oil, sassafras oil, savory oil, schisandra oil, spearmint oil, spikenard, spruce, star anise oil, tangerine, tarragon oil, thyme oil, tsuga, valerian, vetiver oil, western red cedar, wintergreen, yarrow oil, and ylang-ylang.

11. The composite of claim 9, wherein the oil is one or more oil from the group including davana oil eucalyptus oil, lemon oil, lemongrass, orange oil, oregano oil, pine oil, rosemary oil, and mellaluca oil.

12. The composite of claim 9, wherein the oil is mellaluca oil.

13. A biodegradable composite comprising a resin containing soy protein and an extract from the melaleuca plant impregnated into a biodegradable sheet.

14. The composite of claim 13, wherein the oil is present in an amount that is a minimum of about 0.05% and a maximum of about 2% based upon the dry weight of the resin.

15. The composite of claim 13, further comprising a carboxy-containing polysaccharide.

16. The composite of claim 15, wherein the carboxy-containing polymer is selected from the group consisting of agar, gellan, and mixtures thereof.

17. The composite of claim 13, wherein the resin further comprises nanoclay.

18. The composite of claim 13, wherein the resin further comprises, nanofibers and microfibers, wherein the nanofibers and microfibers are biodegradable.

19. The composite of claim 13 wherein the nanofibers and microfibers comprises microfibrillated cellulose and nanofibrillated cellulose.

20. The composition of claim 13, further comprising a plasticizer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 08/87234

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D06P 1/52; B32B 27/12 (2009.01)

USPC - 523/124; 442/123

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)

IPC(8) -- D06P 1/52; B32B 27/12 (2009.01) and USPC -- 523/124; 442/123

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8) -- B32B\$ OR D06P\$ (2009.01) and USPC -- 52/80.1,782.1Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (PGPB,USPT,USOC,EPAB,JPAB); USPTO; Espacenet; Google Patents; Google Scholar; Google -- please see Extra Sheet for Search Terms Used

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2004/0173306 A1 (Thames et al.) 09 September 2004 (09.09.2004) Abstract; [0006]; [0007]; [0014]	1-2 --- 3-20
Y	US 2007/0256247 A1 (Privitera et al.) 08 November 2007 (08.11.2007) Abstract; [0131]; [0133]; [0136]	3-6, 8, 11, 12-20
Y	US 2006/0264135 A1 (Netravali et al.) 23 November 2006 (23.11.2006) Abstract; para [0010]; [0014]; [0039]; [0099]; [0107]; [0108]; [0058]	6-20

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

04 February 2009 (04.02.2009)

Date of mailing of the international search report

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Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 08/87234

Search Terms Used:

BIODEGRADABLE; COMPOSITE; ESSENTIAL OIL; MELALEUCA; RESIN; SOY PROTEIN OR SOYA PROTEIN OR SOYBEAN PROTEIN OR SOY-BASED NEAR5 PROTEIN; TEA TREE OIL; TERPINEN-4-OL, TERPINENOL-4, 1-TERPINEN-4-OL, 4-TERPINEOL

agar oil, ajwain oil, angelica root oil, anise oil, balsam oil, basil oil, buchu oil, bergamot oil, black pepper oil, cannabis flower essential oil, caraway oil, cardamom seed oil, carrot seed oil, cedarwood oil, chamomile oil, cinnamon oil, cistus oil, citronella oil, clary sage, clove leaf oil, coriander oil, costmary oil, cranberry seed oil, cumin oil (black seed oil), cypress oil, davana oil, dill oil, eucalyptus oil, fennel seed oil, fenugreek oil, fir oil, frankincense oil, galbanum, geranium oil, ginger oil, goldenrod, grapefruit oil, henna oil, helichrysum, hyssop, idaho tansy, jasmine oil, juniper berry oil, lavender oil, ledum, lemon oil, lemongrass, litsea cubeba oil, maijoram, melaleuca oil (tea tree oil), melissa oil (lemon balm), mentha arvensis oil (mint oil), mountain savory, mustard oil, myrrh oil, myrtle, neroli, nutmeg, orange oil, oregano oil, orris oil, palo santo, parsley oil, patchouli oil, perilla, peppermint oil, petitgrain, pine oil, ravensara, red cedar, roman chamomile, rose oil, rosehip oil, rosemary oil, rosewood oil, sage oil, sandalwood oil, sassafras oil, savory oil, schisandra oil, spearmint oil, spikenard, spruce, star anise oil, tangerine, tarragon oil, thyme oil, tsuga, valerian, vetiver oil, western red cedar, wintergreen, yarrow oil, and ylang-ylang

hemp kenaf sorghum jute flax sisal banana kapok bamboo ramie pineapple

davana oil eucalyptus oil lemon oil lemongrass orange oil oregano oil pine oil rosemary oil mellaluca oil