FUNGAL TEXTILE MATERIALS AND LEATHER ANALOGS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority of U.S. Provisional Patent Applications 62/862,860, filed 18 June 2019; 62/951,332, filed 20 December 2019; and 62/966,525, filed 27 January 2020, all of which are incorporated by reference herein in their entireties.

FIELD OF THE INVENTION

This invention relates generally to fungal materials, and particularly to materials derived from filamentous fungi that can be used as leather analogs and in other textiles and fabrics.

BACKGROUND OF THE INVENTION

Many current textile materials, including but not limited to leather, create environmental problems during manufacturing and may be difficult or impossible to recycle or dispose of in an environmentally safe way at the end of an article's useful life. By way of non-limiting example, the manufacture of leather depends on the rearing of cattle (which has a significant environmental impact in itself and may raise animal welfare concerns) and requires a tanning step, which may use highly toxic chemicals such as chromium, formic acid, mercury, and various solvents. Leather also biodegrades slowly, over times of about 25 to about 40 years. Many textile materials suffer from similar environmental or ethical concerns.

There is thus a need in the art for textile materials that may be produced cost-effectively with a minimum of environmental impact and without animal welfare or other ethical concerns. It is further advantageous for such materials to retain various physical and/or mechanical properties, e.g. tensile strength, tear strength, flexural rigidity, elasticity, texture, thermal properties, sensory attributes, etc., of conventional textile materials, e.g. leather.

SUMMARY ~~OF THE INVENTION~~

In one ~~aspect~~example of the present ~~invention~~disclosure, a method for preparing a durable sheet material comprising fungal biomass comprises (a) causing a solution to infiltrate an inactivated fungal biomass, the solution comprising a solvent and a component selected from the group consisting of a polymer, a crosslinker, and combinations and mixtures thereof; and (b) curing the biomass to remove solvent from the biomass and form the durable sheet material.

In ~~embodiment~~examples, the fungal biomass may comprise fungal mycelia.

In ~~embodiment~~examples, the inactivated fungal biomass may be size-reduced prior to step (a) and step (a) may comprise blending the size-reduced inactivated fungal biomass with the solution to form a blended composition. The method may, but need not, further comprise, casting the blended composition to form a cast sheet from which solvent is removed in step (b). The size-reduced inactivated fungal biomass may, but need not, have an average particle size of no more than about 125 microns.

In ~~embodiment~~examples, the inactivated fungal biomass may comprise a cohesive fungal biomass and (a) may comprise agitating the inactivated fungal biomass and the solution together for a time period. The cohesive fungal biomass may, but need not, be produced by a surface fermentation process or a submerged solid surface fermentation process. The time period may, but need not, be selected from the group consisting of at least about 4 hours, at least about 5 hours, at least about 10 hours, at least about 15 hours, at least about 20 hours, or at least about 25 hours. The time period may, but need not, be between about 10 hours and about 20 hours. The agitating may, but need not, be carried out at a pressure other than atmospheric pressure, which may be sub-atmospheric pressure or super-atmospheric pressure. The method may, but need not, further comprise subjecting the inactivated fungal biomass to treatment with at least one chemical selected from the group consisting of calcium hydroxide and tannins.

In ~~embodiment~~examples, the inactivated fungal biomass may comprise a fungal paste produced by submerged fermentation.

In ~~embodiment~~examples, the polymer may be selected from the group consisting of polyvinyl alcohol, chitosan, polyethylene glycol, alginates, starches, polycaprolactones, polyacrylic acids, hyaluronic acid, and combinations thereof.

In ~~embodiment~~examples, the polymer may be present in the durable sheet material in an amount selected from the group consisting of no more than about 25 wt% of the durable sheet material, no more than about 20 wt% of the durable sheet material, no more than about 15 wt% of the durable sheet material, no more than about 10 wt% of the durable sheet material, and no more than about 5 wt% of the durable sheet material.

In ~~embodiment~~examples, the crosslinker may be selected from the group consisting of citric acid, tannic acid, suberic acid, adipic acid, succinic acid, extracted vegetable tannins, glyoxal, and combinations thereof.

In ~~embodiment~~examples, the solution may further comprise a plasticizer. The plasticizer may, but need not, be selected from the group consisting of glycerol and esters thereof,

polyethylene glycol, citric acid, oleic acid, oleic acid polyols and esters thereof, epoxidized triglyceride vegetable oils, castor oil, pentaerythritol, fatty acid esters, carboxylic ester-based plasticizers, trimellitates, adipates, sebacates, maleates, biological plasticizers, and combinations thereof.

In ~~embodiment~~examples, the fungal biomass may comprise at least one filamentous fungus belonging to an order selected from the group consisting of *Ustilaginales*, *Russulales*, *Agaricales*, *Pezizales*, and *Hypocreales*.

In ~~embodiment~~examples, the fungal biomass may comprise at least one filamentous fungus belonging to a family selected from the group consisting of *Ustilaginaceae*, *Hericiaceae*, *Polyporaceae*, *Grifolaceae*, *Lyophyllaceae*, *Strophariaceae*, *Lycoperdaceae*, *Agaricaceae*, *Pleurotaceae*, *Physalacriaceae,* *Omphalotaceae,* *Tuberaceae*, *Morchellaceae*, *Sparassidaceae*, *Nectriaceae*, and *Cordycipitaceae*.

In ~~embodiment~~examples, the fungal biomass may comprise at least one filamentous fungus belonging to a genus selected from the group consisting of *Agaricus*, *Calocybe*, *Calvatia*, *Cordyceps*, *Disciotis*, *Fomes*, *Fusarium*, *Ganoderma*, *Grifola*, *Hericulum*, *Hypholoma*, *Hypsizygus*, *Morchella*, *Pholiota*, *Pleurotus*, *Polyporous*, *Sparassis*, *Stropharia*, *Tuber*, and *Ustilago*.

In ~~embodiment~~examples, the fungal biomass may comprise at least one filamentous fungus selected from the group consisting of *Ustilago esculenta*, *Hericulum erinaceus*, *Polyporous squamosus*, *Grifola fondosa*, *Hypsizygus marmoreus*, *Hypsizygus ulmarius*, *Calocybe gambosa*, *Pholiota nameko*, *Calvatia gigantea*, *Agaricus bisporus*, *Stropharia rugosoannulata*, *Hypholoma lateritium*, *Pleurotus eryngii*, *Pleurotus ostreatus*, *Pleurotus ostreatus* var. *columbinus*, *Tuber borchii*, *Morchella esculenta*, *Morchella conica*, *Morchella importuna*, *Sparassis crispa*, *Fusarium venenatum*, MK7 ATCC Accession Deposit No. PTA-10698, *Disciotis venosa*, and *Cordyceps militaris*.

In ~~embodiment~~examples, the solution may further comprise at least one of a pigment, a solubilizer, and a pH adjusting agent. The solubilizer may, but need not, be selected from the group consisting of hydrochloric acid, acetic acid, formic acid, lactic acid, and combinations and mixtures thereof. The pH adjusting agent may, but need not, be selected from the group consisting of hydrochloric acid, acetic acid, formic acid, lactic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the durable sheet material may comprise proteins crosslinked with isopeptide bonds.

In ~~embodiment~~examples, the method may further comprise at least one of (i) adding a thermal dopant to the inactivated fungal biomass and (ii) adding a thermal dopant to the durable sheet material after step (b). An amount of the thermal dopant may, but need not, be selected from the group consisting of at least about 2.5 wt% of the durable sheet material, at least about 5 wt% of the durable sheet material, at least about 7.5 wt% of the durable sheet material, at least about 10 wt% of the durable sheet material, at least about 12.5 wt% of the durable sheet material, at least about 15 wt% of the durable sheet material, and at least about 17.5 wt% of the durable sheet material. An amount of the thermal dopant may, but need not, be selected from the group consisting of no more than about 20 wt% of the durable sheet material, no more than about 17.5 wt% of the durable sheet material, no more than about 15 wt% of the durable sheet material, no more than about 12.5 wt% of the durable sheet material, no more than about 10 wt% of the durable sheet material, no more than about 7.5 wt% of the durable sheet material, and no more than about 5 wt% of the durable sheet material. The thermal dopant may, but need not, be selected from the group consisting of a ceramic material, a metallic material, a polymeric material, and combinations thereof. The thermal dopant may, but need not, be selected from the group consisting of activated charcoal, aluminum oxide, bentonite, diatomaceous earth, ethylene vinyl acetate, lignin, nanosilica, polycaprolactone, polylactic acid, silicone, and yttrium oxide.

In ~~embodiment~~examples, the inactivated fungal biomass may be a size-reduced inactivated fungal biomass.

In ~~embodiment~~examples, the inactivated fungal biomass may comprise a biomat, or portion thereof, produced by a surface fermentation process. A carbon-to-nitrogen molar ratio in a growth medium of the surface fermentation process may, but need not, be between about 5 and about 20, or between about 7 and about 15.

In another ~~aspect~~example of the present ~~invention~~disclosure, a textile composition comprises an inactivated fungal biomass; and at least one component selected from the group consisting of a plasticizer, a polymer, a crosslinker, and a dye, wherein the at least one component is distributed in the fungal mycelial biomass.

In one aspect, the present disclosure refers to a textile composition, comprising: an inactivated fungal biomass; and a polymer, wherein the polymer is infiltrated into the inactivated fungal biomass to a fungal biomass:polymer loading ratio of between about 25:75 and about 75:25, and wherein the textile composition has a tensile strength of at least about 2 MPa.

In ~~embodiment~~examples, the textile composition may have a thickness of at least about 1 mm.

In ~~embodiment~~examples, the textile composition may have a tear force of at least about 30 N.

In ~~embodiment~~examples, the textile composition may have a tear strength of at least about 10 N/mm.

In ~~embodiment~~examples, the textile composition may have a flexural rigidity of no more than about 5 gram-centimeters.

In ~~embodiment~~examples, the textile composition may have a tensile strength of at least about 10 MPa.

In ~~embodiment~~examples, the textile composition may have a water spotting grey scale rating of at least about 3.

In ~~embodiment~~examples, the textile composition may have a light color fastness blue wool rating of at least about 4.

In ~~embodiment~~examples, the textile composition may have a rub color fastness grey scale rating, when dry, of at least about 3.

In ~~embodiment~~examples, the textile composition may have a rub color fastness grey scale rating, when wet, of at least about 2.

In ~~embodiment~~examples, the textile composition may further comprise at least one backing layer of a non-fungal textile material. The non-fungal textile material may, but need not, be selected from the group consisting of an acrylic textile, an alpaca textile, an angora textile, a cashmere textile, a coir textile, a cotton textile, an eisengarn textile, a hemp textile, a jute textile, a Kevlar textile, a linen textile, a microfiber textile, a mohair textile, a nylon textile, an olefin textile, a pashmina textile, a polyester textile, a piña textile, a ramie textile, a rayon textile, a sea silk textile, a silk textile, a sisal textile, a spandex textile, a spider silk textile, a wool textile, and combinations and mixtures thereof.

In one aspect, the present disclosure refers to a textile composition, comprising: an inactivated fungal biomass; a polymer; and at least one backing layer of a non-fungal textile material, wherein the polymer is infiltrated into the inactivated fungal biomass to a fungal biomass:polymer loading ratio of between about 25:75 and about 75:25.

In ~~embodiment~~examples, the textile composition may further comprise a thermal dopant. T thermal dopant may, but need not, be selected from the group consisting of a ceramic material, a metallic material, a polymeric material, and combinations and mixtures thereof. The thermal dopant may, but need not, be selected from the group consisting of activated charcoal, aluminum oxide, bentonite, diatomaceous earth, ethylene vinyl acetate, lignin, nanosilica, polycaprolactone, polylactic acid, silicone, and yttrium oxide. A thermal characteristic of the textile composition may, but need not, be altered relative to the same thermal characteristic of the textile composition in the absence of the thermal dopant, wherein the thermal characteristic is selected from the group consisting of thermal effusivity, thermal conductivity, heat capacity, and combinations thereof.

In one aspect, the present disclosure refers to a textile composition, comprising: an inactivated fungal biomass; a polymer; and a thermal dopant, wherein the polymer is infiltrated into the inactivated fungal biomass to a fungal biomass:polymer loading ratio of between about 25:75 and about 75:25.

In another ~~aspect~~example of the present ~~invention~~disclosure, an article of manufacture comprises a textile composition as described herein, wherein the article of manufacture is selected from the group consisting of an article of clothing, an accessory item, and a furniture item.

In another ~~aspect~~example of the present ~~invention~~disclosure, a method for making a durable sheet material comprises (a) contacting an inactivated fungal biomass with an aqueous solution comprising calcium hydroxide to form a limed inactivated fungal biomass; (b) contacting the limed inactivated fungal biomass with an aqueous solution comprising ammonium sulfate to form a delimed inactivated fungal biomass; (c) contacting the delimed inactivated fungal biomass with an aqueous solution comprising a polymer to form a pickled inactivated fungal biomass; (d) contacting the pickled inactivated fungal biomass with an aqueous solution comprising a crosslinker to form a tanned inactivated fungal biomass; (e) contacting the tanned inactivated fungal biomass with an aqueous solution comprising a plasticizer to form a plasticized inactivated fungal biomass; (f) drying the plasticized inactivated fungal biomass to form a dried inactivated fungal biomass; and (g) heat-pressing the dried inactivated fungal biomass to form the durable sheet material.

In ~~embodiment~~examples, the method may further comprise, between any pair of steps selected from the group consisting of steps (a) and (b), steps (b) and (c), steps (c) and (d), and steps (d) and (e), rinsing the inactivated fungal biomass with water to remove residual aqueous solution.

In ~~embodiment~~examples, at least one of steps (a) through (e) may comprise agitating the inactivated fungal biomass with the aqueous solution.

In ~~embodiment~~examples, the aqueous solution of at least one of steps (a) through (c) may further comprise a surfactant or solubilizer. The surfactant or solubilizer may, but need not, be selected from the group consisting of polysorbates, hydrochloric acid, acetic acid, formic acid, lactic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the polymer may be selected from the group consisting of polyvinyl alcohol, chitosan, polyethylene glycol, alginates, starches, polycaprolactones, polyacrylic acids, hyaluronic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the aqueous solution of step (c) may further comprise a plasticizer selected from the group consisting of glycerol and esters thereof, polyethylene glycol, citric acid, oleic acid, oleic acid polyols and esters thereof, epoxidized triglyceride vegetable oils, castor oil, pentaerythritol, fatty acid esters, carboxylic ester-based plasticizers, trimellitates, adipates, sebacates, maleates, biological plasticizers, and combinations and mixtures thereof.

In ~~embodiment~~examples, the aqueous solution of step (c) may further comprise an alkali metal halide. The alkali metal halide may, but need not, be sodium chloride.

In ~~embodiment~~examples, the crosslinker may be selected from the group consisting of citric acid, tannic acid, suberic acid, adipic acid, succinic acid, extracted vegetable tannins, glyoxal, and combinations and mixtures thereof.

In ~~embodiment~~examples, the plasticizer may be selected from the group consisting of glycerol and esters thereof, polyethylene glycol, citric acid, oleic acid, oleic acid polyols and esters thereof, epoxidized triglyceride vegetable oils, castor oil, pentaerythritol, fatty acid esters, carboxylic ester-based plasticizers, trimellitates, adipates, sebacates, maleates, biological plasticizers, and combinations and mixtures thereof.

In another ~~aspect~~example of the present ~~invention~~disclosure, a method for making a durable sheet material comprises (a) inactivating a fungal biomass by boiling the biomass in water; (b) contacting the inactivated fungal biomass with an aqueous solution comprising calcium hydroxide to form a limed inactivated fungal biomass; (c) contacting the limed inactivated fungal biomass with an aqueous solution comprising ammonium sulfate to form a delimed inactivated fungal biomass; (d) contacting the delimed inactivated fungal biomass with an aqueous solution comprising an alkali metal halide to form a pickled inactivated fungal biomass; (e) contacting the pickled inactivated fungal biomass with a first crosslinker to form a tanned inactivated fungal biomass; (f) contacting the tanned inactivated fungal biomass with an aqueous solution comprising at least one of a second crosslinker and a polymer to form a re-tanned inactivated fungal biomass; (g) contacting the re-tanned inactivated fungal biomass with a fatliquoring oil to form a fatliquored inactivated fungal biomass; (h) adhering a non-fungal textile backing to the inactivated fungal biomass to form a backed inactivated fungal biomass; (i) heat-pressing the backed inactivated fungal biomass to form a heat-pressed inactivated fungal biomass; (j) drying the heat-pressed inactivated fungal biomass to form a dried inactivated fungal biomass; and (k) applying at least one of a finishing wax, a finishing oil, and nitrocellulose to the dried inactivated fungal biomass to form the durable sheet material.

In ~~embodiment~~examples, the method may further comprise, between any pair of steps selected from the group consisting of steps (b) and (c), steps (c) and (d), and steps (e) and (f), rinsing the inactivated fungal biomass with water to remove residual aqueous solution.

In ~~embodiment~~examples, at least one of steps (a) through (g) may comprise agitating the inactivated fungal biomass with the aqueous solution.

In ~~embodiment~~examples, the aqueous solution of at least one of steps (b) and (c) may further comprise a surfactant or solubilizer. The surfactant or solubilizer may, but need not, be

selected from the group consisting of polysorbates, hydrochloric acid, acetic acid, formic acid, lactic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the polymer may, but need not, be selected from the group consisting of polyvinyl alcohol, chitosan, polyethylene glycol, alginates, starches, polycaprolactones, polyacrylic acids, hyaluronic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the alkali metal halide may be sodium chloride.

In ~~embodiment~~examples, the aqueous solution of at least one of steps (d) through (f) may comprise a pH adjusting agent. The pH adjusting agent may, but need not, comprise hydrochloric acid, acetic acid, formic acid, lactic acid, or a combination or mixture thereof, or a metal hydroxide.

In ~~embodiment~~examples, the first crosslinker may comprise an aluminum salt, a chromium salt, a titanium salt, an aldehyde, or a combination or mixture thereof. The first crosslinker may, but need not, be an aluminum silicate.

In ~~embodiment~~examples, the second crosslinker may be selected from the group consisting of citric acid, tannic acid, suberic acid, adipic acid, succinic acid, extracted vegetable tannins, glyoxal, and combinations and mixtures thereof.

In ~~embodiment~~examples, the polymer may be selected from the group consisting of polyvinyl alcohol, chitosan, polyethylene glycol, alginates, starches, polycaprolactones, polyacrylic acids, hyaluronic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the aqueous solution of step (f) may further comprise an anionic dye.

In ~~embodiment~~examples, the fatliquoring oil may be selected from the group consisting of sulfated castor oil, beeswax, coconut oil, vegetable oil, olive oil, linseed oil, oleic acid, and combinations and mixtures thereof.

In ~~embodiment~~examples, the fatliquoring oil may comprise an emulsion and the method may further comprise, between steps (g) and (h), contacting the fatliquoring oil with an acid to dissociate the emulsion.

In ~~embodiment~~examples, the finishing wax may be selected from the group consisting of carnauba wax, candelilla wax, and combinations and mixtures thereof.

~~Embodiment~~Examples of the present ~~invention~~disclosure generally relate to production of durable sheet materials comprising fungal biomass. In certain ~~embodiment~~examples, durable sheet materials may have controlled, engineered, and/or tuned thermal properties. By way of first non-limiting example, thermal properties of durable sheet materials of the present ~~invention~~disclosure may be

controlled, engineered, and/or tuned by controlling the size, number, and/or spatial distribution of air bubbles in the durable sheet material. By way of second non-limiting example, thermal properties of durable sheet materials of the present ~~invention~~disclosure may be controlled, engineered, and/or tuned by adding a thermal dopant having a desired thermal property (e.g. heat capacity, thermal conductivity, thermal effusivity, and combinations thereof) and thus modifying the same thermal property of the durable sheet material as a whole. By way of third non-limiting example, thermal properties of durable sheet materials of the present ~~invention~~disclosure may be controlled, engineered, and/or tuned by controlling the mass, volume, thickness, spatial distribution, etc. of thermal dopants included in the durable sheet material, thereby providing for an engineered or designed spatial pattern of heat exchange in and through the durable sheet material.

~~Embodiment~~Examples of the present ~~invention~~disclosure provide for the manufacture of fungal textile materials, and particularly fungal leather analogs, from intact cohesive fungal biomasses (e.g. fungal biomats produced by surface fermentation or any other suitable process), size-reduced or homogenized fungal biomasses, or any other physical form of fungal biomass, especially filamentous fungal biomass. The materials of the present ~~invention~~disclosure generally include both an inactivated fungal biomass and a component selected from the group consisting of a polymer, a plasticizer, a crosslinker, and a dye, and the methods of the present ~~invention~~disclosure allow for the introduction of such component(s) to the inactivated fungal biomass to produce materials having desired chemical, physical, and/or thermal properties. The materials of the present ~~invention~~disclosure may generally be provided as durable sheet materials suitable for use in the same or similar applications as conventional textiles.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a generalized schematic of a method for making a fungal textile material, according to embodiments of the present invention.

Figure 2 is a generalized schematic of a method for making a fungal textile material, according to embodiments of the present invention.

Figure 3 is a generalized schematic of a method for making a fungal textile material, according to embodiments of the present invention.

Figure 4 is a generalized schematic of a method for making a fungal textile material, according to embodiments of the present invention.

Figure 5 is a generalized schematic of a method for making a fungal textile material, according to embodiments of the present invention.