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(54) Titre : COMPOSITION THERMOPLASTIQUE
(54) Title: THERMOPLASTIC COMPOSITION

(57) **Abrégé/Abstract:**

The objective of the present invention is to provide: a material that is a cellulose-based composition, is thermoplastic, and does not require the disposal of a solvent or the use of environmentally hazardous substances such as halide-containing substances during the manufacturing process; and a method for producing the same. The thermoplastic composition contains cellulose and a eutectic mixture of monosaccharide and/or disaccharide and hydroxycarboxylic acid. The method for manufacturing a thermoplastic composition comprises: a first step for mixing hydroxycarboxylic acid and monosaccharide and/or disaccharide at a temperature of 150-240 °C; and a second step for mixing the mixture obtained in the first step and cellulose at a temperature of 150-240 °C. In addition, the method for manufacturing a thermoplastic composition comprises a step for mixing cellulose, hydroxycarboxylic acid and monosaccharide and/or disaccharide in an extruder at a temperature of 150-240 °C. The eutectic mixture is preferably a mixture of lactic acid and glucose. In addition, the cellulose content is preferably 0.05-60.0 mass%.

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Abstract:

The present invention intends to provide a composition that is cellulose-based but thermoplastic and can be manufactured without disposing a solvent or using environmentally hazardous substances such as halide-containing substances; and a method for producing the same. The thermoplastic composition contains cellulose and a eutectic mixture of monosaccharide and/or disaccharide and hydroxycarboxylic acid. The method for manufacturing a thermoplastic composition comprises: a first step of mixing hydroxycarboxylic acid and monosaccharide and/or disaccharide at a temperature of 150-240 °C; and a second step of mixing the mixture obtained in the first step and cellulose at a temperature of 150-240 °C. In addition, the method for manufacturing a thermoplastic composition comprises a step of mixing cellulose, hydroxycarboxylic acid and monosaccharide and/or disaccharide in an extruder at a temperature of 150-240 °C. The eutectic mixture is preferably a mixture of lactic acid and glucose. In addition, the cellulose content is preferably 0.05-60.0 mass%.

DESCRIPTION

Title of the Invention: THERMOPLASTIC COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to a cellulose-based thermoplastic composition, specifically, a thermoplastic composition containing cellulose and an eutectic mixture of a hydroxycarboxylic acid and a sugar.

BACKGROUND ART

[0002]

In recent years, biomass-derived materials have been attracting attention against a backdrop of issues such as global environmental protection or oil depletion, etc. From an environmental standpoint, plastic waste has also been perceived as a problem, increasing importance of biodegradable thermoplastic materials. Cellulose is one of representative biomass-derived materials and conventionally has been heavily used. In particular, since plant-derived cellulose is also biodegradable, it is attracting attention again from an environmental standpoint. Recently, several studies have begun to examine new use of such cellulose as a resin-like material.

[0003]

For example, Patent Document 1 discloses a method for producing a nanocellulose material in which a cellulosic

fibrous material such as pulp is swollen and suspended in the presence of a deep eutectic solvent and water, treated with sodium hydroxide, etc., filtered and washed, and then homogenized at high pressure. The deep eutectic solvent is a solvent that is liquid at room temperature and that is obtained by mixing a hydrogen bond donor compound with a hydrogen bond acceptor compound in a certain ratio. A solvent with any physical property can be created by combining the donor compound and the acceptor compound, and various combinations have been reported (e.g., Non-Patent Document 1). Since the deep eutectic solvent generally has excellent solubility, cellulose, etc. can be microdispersed therein. Furthermore, a colloidal solution of a nanocellulose fiber can be made depending on a combination of raw materials. In Patent Document 1, a urea/choline chloride-based deep eutectic solvent is used.

[0004]

Non-patent Document 2 discloses a technique for producing a wood-based fiber by dispersing bleached birch pulp in a reactive or non-reactive deep eutectic solvent such as urea/ammonium thiocyanate, urea/sulfamic acid, or glycerol/aminoguanidine hydrochloride deep eutectic solvent, followed by filtering and washing. Non-patent Document 3 discloses a technique for producing a film with various mechanical properties by dispersing sawdust in an imidazole/triethylammonium chloride deep eutectic solvent, treating the resulting dispersion with anhydrous succinic

acid, and then filtering and drying the resulting suspension. Such technology makes it possible to produce a resin-like material from a cellulosic material, such as discarded paper and thus can contribute to waste reduction.

Citation List

Patent Document

[0005]

Patent Document 1: Japanese Unexamined Patent Application (Translation of PCT Application), Publication No. 2020-518715

Non-Patent Document

[0006]

Non-Patent Document 1: L. Wils, et al., *Molecules*, 26, 6556-6575 (2021)

Non-Patent Document 2: P. Li, *ACTA UNIVERSITATIS OULUENSIS, C Technica* 739(2020)

Non-Patent Document 3: J. Antti Sirvio, et al., *Cellulose*, 28, 6881-6898 (2021)

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0007]

As described above, a resin-like material can be obtained from cellulose using a deep eutectic solvent, but the thus-obtained conventional materials are not thermoplastic and their applications tend to be limited. Also, in the techniques described in Patent Document 1 and Non-Patent Documents 2 and 3, the thus-prepared cellulose materials are all formed as

films on filters by filtration. This not only requires time-consuming preparation, but also causes a problem of disposal of the deep eutectic solvent. These technologies also use a sulfur-containing strong acid compound such as sulfamic acid or a chloride as the deep eutectic solvent, and there is room for improvement from an environmental standpoint.

[0008]

In order to solve the above problems, an object of the present invention is to provide a material that is thermoplastic while being a cellulose-based composition, and that does not require disposal of a solvent or use of an environmentally hazardous substance such as a halide-containing substance in a manufacturing process; and a method for manufacturing the material.

Means for Solving the Problems

[0009]

The present inventors conducted extensive studies to achieve the above object and have found that a composition containing cellulose and an eutectic mixture of a monosaccharide and/or a disaccharide and a hydroxycarboxylic acid has a resin-like property, exhibits thermoplasticity, and can be produced without disposal of a solvent or use of an environmentally hazardous substance. Thus, the present invention has been completed.

[0010]

That is, the present invention provides the following aspects (1) to (11).

(1) A thermoplastic composition including: cellulose; and an eutectic mixture of a monosaccharide and/or a disaccharide and a hydroxycarboxylic acid.

(2) The thermoplastic composition according to (1), in which the eutectic mixture is a mixture of lactic acid and glucose.

(3) The thermoplastic composition according to (1) or (2), further comprising hemicellulose and/or lignin, wherein the cellulose is plant-derived cellulose.

(4) The thermoplastic composition according to any one of (1) to (3), in which the composition includes 0.05 to 60.0% by mass of the cellulose.

(5) The thermoplastic composition according to any one of (1) to (4), in which the composition has a mass ratio of the hydroxycarboxylic acid : the monosaccharide and/or the disaccharide in a range of 1:2 to 6:1.

(6) The thermoplastic composition according to any one of (1) to (5), further including one or more substances selected from the group consisting of an inorganic filler, a natural thermoplastic resin, a synthetic thermoplastic resin, and a biodegradable resin.

(7) A method for producing a thermoplastic composition, the method including:

mixing a hydroxycarboxylic acid and a monosaccharide and/or a disaccharide at a temperature of 150 to 240°C (first step); and

mixing the mixture obtained in the first step and cellulose at a temperature of 150 to 240°C (second step).

(8) The method for producing a thermoplastic composition according to (7), further including kneading and molding the mixture obtained in the second step in an extruder (third step).

(9) A method for producing a thermoplastic composition, the method including mixing cellulose, a hydroxycarboxylic acid, and a monosaccharide and/or a disaccharide in an extruder at a temperature of 150 to 240°C.

(10) A thermoplastic pellet formed of the thermoplastic composition according to any one of (1) to (6).

(11) A molded product formed of the thermoplastic composition according to any one of (1) to (6).

Effects of the Invention

[0011]

A thermoplastic composition of the present invention is thermoplastic while being a cellulose-based composition and thus has a good mechanical property derived from the cellulose and excellent moldability. Therefore, the thermoplastic composition is suitable as a material for various molded products and is useful as an industrial material such as a thermoplastic pellet. In addition, the thermoplastic composition has an advantage of not requiring disposal of a solvent or use of an environmentally hazardous substance such as a halide-containing substance in a manufacturing process. Furthermore, the thermoplastic composition of the present invention and a method for producing the thermoplastic composition can be utilized for waste disposal since cellulose

containing an impurity, for example, wood waste such as sawdust or waste paper can also be used as a raw material. Therefore, the composition and the method are useful from the perspective of global environmental conservation

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0012]

The present invention will be described in detail with reference to embodiments.

[0013]

[Thermoplastic composition]

A first aspect of the present invention is a thermoplastic composition including cellulose; and an eutectic mixture of a monosaccharide and/or a disaccharide, together with a hydroxycarboxylic acid. First, these components will be described in detail. Note that, the phrase "monosaccharide and/or disaccharide", as used herein, may be collectively referred to as "sugar".

[0014]

<Cellulose>

Cellulose constituting a thermoplastic composition of the present invention is not particularly limited, and various known cellulose may be used. Examples thereof include, but are not limited to, natural cellulose derived from, for example, a plant; modified cellulose including cellulose acetate, carboxymethyl cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, or

hydroxypropylmethyl cellulose; or regenerated cellulose.

Furthermore, the cellulose may be included in not only wood pulp or non-wood pulp, but also those less refined, or even waste such as sawdust, waste wood, or waste paper.

[0015]

The cellulose is a polysaccharide, a type of carbohydrate, and a main component of plant fiber. The cellulose is usually present in a plant as lignocellulose bound to or mixed with hemicellulose or lignin. In general, a plant-derived cellulose fiber has a configuration in which bundles of 30 to 40 molecules of cellulose form ultrafine, highly crystalline microfibrils with a diameter of about 3 nm and a length of several hundred nanometers to several tens of micrometers and the microfibrils are further bundled together via soft non-crystalline portions.

[0016]

The cellulose constituting the thermoplastic composition of the present invention is preferably plant-derived cellulose. The composition of the present invention exhibits a resin-like property and thermoplasticity even if the cellulose is, for example, the above-described lignocellulose. Therefore, pulp, etc. can be used without refining, and waste such as waste paper can be used as a raw material. In one preferred embodiment of the present invention, the cellulose is plant-derived and further includes hemicellulose and/or lignin.

[0017]

The plant-derived cellulose is not particularly limited. Examples include, but are not limited to, those derived from wood, bamboo, hemp, jute, kenaf, and agricultural waste including wheat or rice straw, corn, a stem of cotton, or sugar cane. Cellulose derived from sawdust, wood chips, waste wood, waste paper, waste cloth, re-formed bedding cotton, recycled pulp, etc. may also be used. Depending on an application of the thermoplastic composition, wood-derived cellulose, especially wood pulp, is generally preferred from the viewpoints of appearance, a mechanical property, and quality stability of the composition, and easy availability of raw materials. The wood pulp is advantageous in terms of a small seasonal fluctuation in supply, and cost.

[0018]

As desired, hemicellulose or lignin may be removed from the plant-derived cellulose. For example, kraft pulp, highly pure cellulose that has been chemically treated with caustic soda to remove hemicellulose and lignin, may be used.

[0019]

In the thermoplastic composition of the present invention, a portion of hydroxy groups in a cellulose molecule may be acetylated or carboxylated or a hydrogen atom in the hydroxy group may be substituted with a metal ion such as sodium or potassium, or an ammonium ion.

[0020]

A content of the cellulose is preferably about 0.05 to 60.0% by mass, more preferably about 0.1 to 50.0% by mass, and

further preferably about 0.2 to 40.0% by mass relative to 100% by mass of a total thermoplastic composition of the present invention. The thermoplastic composition of the present invention exhibits texture or excellent mechanical strength resulting from cellulose even when the content of the cellulose is as small as about 0.05% by mass. Furthermore, satisfactory thermoplasticity is ensured when the content of the cellulose is about 60.0% by mass or less. Note that, when the thermoplastic composition of the present invention contains hemicellulose and/or lignin, these components are materials constituting lignocellulose, so amounts thereof shall be included in the content of the cellulose.

[0021]

Herein, the content of the cellulose is preferably about 0.05 to 20.0% by mass, particularly 0.1 to 10.0% by mass, further 0.2 to 5.0% by mass, and especially 0.4 to 2.0% by mass relative to 100% by mass of a total thermoplastic composition of the present invention in order to improve molding processability of the thermoplastic composition or when the thermoplastic composition is produced in a small amount in a low-shear mixer. On the other hand, the content is preferably about 5.0 to 60.0% by mass, for example, 10.0 to 50.0% by mass, particularly 15.0 to 40.0% by mass, further 18.0 to 30.0% by mass, and especially 20.0 to 25.0% by mass in order to improve heat resistance or a mechanical property of the thermoplastic composition or from the viewpoint of utilizing more cellulose waste.

[0022]

<Eutectic mixture>

The thermoplastic composition of the present invention contains, in addition to the above-described cellulose, an eutectic mixture of a hydroxycarboxylic acid and a sugar. This eutectic mixture can act like a deep eutectic solvent, loosening cellulose to near a level of a nanofiber and even dissolving or microdispersing it to form a nearly homogeneous mixture. This eutectic mixture can also form a composition that is solid at room temperature and is thermoplastic when mixed with cellulose, etc. This is an unexpected phenomenon that does not occur in the above-described deep eutectic solvent such as imidazole/ammonium chloride. The reason why the composition of the invention results in such a thermoplastic material is unknown, but it is believed that a hydroxycarboxylic acid and a sugar may interact with cellulose at the same time that they form a eutectic crystal. However, the present invention is not limited to a certain theory.

[0023]

In the present invention, the eutectic mixture forms a thermoplastic composition together with cellulose as described above, and does not need to be separated and removed after a cellulose material is prepared (for example, as in the preparation method described in Non-Patent document 2). Therefore, labor and cost for separation, waste solvent treatment, etc. can be reduced. The eutectic mixture in the thermoplastic composition of the present invention is

constituted of halogen-free natural products, that is, a hydroxycarboxylic acid and a monosaccharide and/or a disaccharide. This also is a reason why the eutectic mixture is an excellent material that does not burden the global environment.

[0024]

(Hydroxycarboxylic acid)

A hydroxycarboxylic acid in the present invention may be any compound as long as it forms an eutectic mixture with a monosaccharide and/or a disaccharide, and a type thereof is not particularly limited. Examples thereof include, but are not limited to, an aliphatic hydroxycarboxylic acid such as glycolic acid, lactic acid, tartronic acid, glyceric acid, hydroxybutyric acid, 2-hydroxybutyric acid, 3-hydroxybutyric acid, gamma-hydroxybutyric acid, malic acid, tartaric acid, citramalic acid, citric acid, isocitric acid, leucinic acid, mevalonic acid, pantoic acid, ricinoleic acid, ricinelaidic acid, cerebronic acid, quinic acid, or shikimic acid; an aromatic hydroxycarboxylic acid such as salicylic acid, creosotic acid, vanillic acid, syringic acid, pyrocatechuic acid, resorcylic acid, protocatechuic acid, gentisic acid, orsellinic acid, gallic acid, mandelic acid, benzylic acid, atrolactic acid, cinnamic acid, melilotic acid, phloretic acid, cumaric acid, umbellic acid, caffeic acid, ferulic acid, or sinapic acid, etc. Depending on a combination of a monosaccharide and/or a disaccharide, a plurality of hydroxycarboxylic acids may also be used in combination.

[0025]

The hydroxycarboxylic acid is preferably a compound having one hydroxy group and one carboxy group in a molecule or an aliphatic hydroxycarboxylic acid. More preferably, a hydroxycarboxylic acid having 2 to 4 carbon atoms is used. Such a hydroxycarboxylic acid easily forms a deep eutectic solvent with a monosaccharide or a disaccharide and a composition containing such a hydroxycarboxylic acid and cellulose exhibits good thermoplasticity. Lactic acid is particularly preferred. Note that, lactic acid may be in any form such as a D-form, an L-form, or a DL-form.

[0026]

(Monosaccharide)

A monosaccharide in the present invention may be any compound as long as it forms an eutectic mixture with a hydroxycarboxylic acid, and a type thereof is not particularly limited. Examples thereof include, but are not limited to, aldose such as glyceraldehyde, erythrose, threose, ribose, lixose, xylose, arabinose, allose, talose, gulose, glucose, altrose, mannose, galactose, or idose; ketose such as dihydroxyacetone, erythrulose, xylulose, ribulose, psicose, fructose, sorbose, or tagatose. Depending on a combination with a hydroxycarboxylic acid, a plurality of monosaccharides may also be used in combination.

[0027]

(Disaccharide)

A disaccharide in the present invention is not

particularly limited. Examples thereof include, but are not limited to, sucrose, lactulose, lactose, maltose, trehalose, or cellobiose. It is also possible to use two or more disaccharides in combination or a monosaccharide and a disaccharide in combination.

[0028]

Among the above-described sugars, a monosaccharide is preferred. The disaccharide is more preferably aldose and further preferably aldohexose. Such a monosaccharide easily forms an eutectic mixture with a hydroxycarboxylic acid and a composition containing such a monosaccharide and cellulose exhibits good thermoplasticity. Among aldohexoses, glucose, allose, mannose, or galactose, especially glucose is preferred. In other words, an eutectic mixture constituting the thermoplastic composition of the present invention is especially preferably a mixture of lactic acid and glucose. A monosaccharide such as glucose has several optical isomers, but any structure can be used in the present invention.

[0029]

<Composition of thermoplastic composition>

For the thermoplastic composition of the present invention, contents of a hydroxycarboxylic acid and a sugar are not particularly limited. For example, a mass ratio of the hydroxycarboxylic acid to the sugar may be selected in a range of 1:4 to 99:1. However, in the present invention, the mass ratio of the hydroxycarboxylic acid to the monosaccharide and/or the disaccharide is preferably in a range of 1:2 to

6:1, more preferably in a range of 1:1 to 4:1, and further preferably in a range of 2:1 to 3:1. When the mass ratio is in the above-described range, an eutectic mixture is easily formed and a composition containing them and cellulose exhibits good thermoplasticity. In an especially preferred embodiment of the present invention, lactic acid and glucose are contained in a mass ratio of 1:1 to 4:1, in particular, a mass ratio of 2:1 to 3:1.

[0030]

In one preferred embodiment of the thermoplastic composition of the present invention, cellulose is contained in an amount of 0.05 to 20.0% by mass, a hydroxycarboxylic acid is contained in an amount of 20.0 to 99.0% by mass, and a sugar is contained in an amount of 1.0 to 80.0% by mass; more preferably, cellulose is contained in an amount of 0.1 to 5.0% by mass, a hydroxycarboxylic acid is contained in an amount of 50.0 to 90.0% by mass, and a sugar is contained in an amount of 5.0 to 50.0% by mass; and further preferably cellulose is contained in an amount of 0.2 to 2.0% by mass, a hydroxycarboxylic acid is contained in an amount of 60 to 80% by mass, and a sugar is contained in an amount of 20 to 40% by mass relative to 100% by mass of a total of cellulose, a hydroxycarboxylic acid, and a sugar. Such a composition can make the thermoplastic composition of the present invention be a thermoplastic composition that has, in particular, excellent texture and molding processability, for example, that melts or solidifies at a temperature of 50 to 230°C, typically 60 to

200°C, and especially about 70 to 150°C.

[0031]

In another preferred embodiment of the thermoplastic composition of the present invention, cellulose is contained in an amount of 5 to 60% by mass, a hydroxycarboxylic acid is contained in an amount of 20 to 80% by mass, and a sugar is contained in an amount of 5 to 50% by mass; more preferably, cellulose is contained in an amount of 10 to 50% by mass, a hydroxycarboxylic acid is contained in an amount of 30 to 60% by mass, and a sugar is contained in an amount of 10 to 40% by mass; and further preferably cellulose is contained in an amount of 20 to 45% by mass, a hydroxycarboxylic acid is contained in an amount of 35 to 50% by mass, and a sugar is contained in an amount of 15 to 30% by mass relative to 100% by mass of a total of cellulose, a hydroxycarboxylic acid, and a sugar. Such a composition can make the thermoplastic composition of the present invention be a thermoplastic composition that has, in particular, excellent texture, heat resistance, or mechanical property, for example, that melts or solidifies at a temperature of 150 to 240°C, typically 160 to 230°C, particularly about 170 to 220°C, and especially 180 to 210°C.

[0032]

<Additive>

The thermoplastic composition of the present invention may further contain one or more substances selected from the group consisting of an inorganic filler, a natural thermoplastic

resin, a synthetic thermoplastic resin, and a biodegradable resin, in addition to the cellulose, the hydroxycarboxylic acid, and the sugar as described above. When an inorganic filler is contained, a physical property of the thermoplastic composition, for example, a mechanical property such as hardness or strength, or heat resistance may be controlled. Furthermore, when any of various resins is contained, a melting or solidification temperature, or a physical property of the thermoplastic composition can be also controlled.

[0033]

(Inorganic filler)

An inorganic filler to be incorporated in the thermoplastic composition of the present invention is not particularly limited. Examples thereof include, but are not limited to, a carbonate, a sulfate, a silicate, a phosphate, a borate, an oxide of calcium, magnesium, aluminum, titanium, iron, zinc, barium, etc., or a hydrate thereof in a powder form, specifically calcium carbonate, magnesium carbonate, zinc oxide, titanium oxide, silica, alumina, clay, talc, kaolin, aluminum hydroxide, magnesium hydroxide, aluminum silicate, magnesium silicate, calcium silicate, aluminum sulfate, magnesium sulfate, calcium sulfate, magnesium phosphate, barium sulfate, silica sand, carbon black, zeolite, molybdenum, diatomaceous earth, sericite, shirasu, calcium sulfite, sodium sulfate, potassium titanate, bentonite, wollastonite, dolomite, graphite, etc. The inorganic filler may be synthetic or derived from natural mineral and may be

contained alone or as a combination of two or more thereof. Among them, calcium carbonate, clay, talc, kaolin, etc. are preferred from the viewpoints of safety and cost. Calcium carbonate is especially preferred since it is commercially available in a variety of particle sizes and shapes and one appropriate for a physical property targeted for the thermoplastic composition may be selected. Use of eggshell-derived calcium carbonate from a food factory can contribute to waste reduction.

[0034]

When the inorganic filler is incorporated into the thermoplastic composition of the present invention, a content thereof is not particularly limited, but is preferably about 10 to 400% by mass, further about 20 to 200% by mass, especially about 30 to 100% by mass relative to 100% by mass of a total of cellulose, a hydroxycarboxylic acid, and a sugar. Such a content allows a physical property such as hardness to be controlled without impairing a melt processability of the thermoplastic composition.

[0035]

(Resin)

A natural thermoplastic resin, a synthetic thermoplastic resin, or a biodegradable resin to be incorporated in the thermoplastic composition of the present invention is not particularly limited. Examples thereof include, but are not limited to, a polyolefin resin such as a polyethylene resin, a polypropylene resin, polymethyl-1-pentene, or an ethylene-

cyclic olefin copolymer; a functional group-containing polyolefin resin such as an ethylene-vinyl acetate copolymer, an ethylene-acrylic acid copolymer, an ethylene-methacrylic acid copolymer, a metal salt of an ethylene-(meth)acrylic acid copolymer (ionomer), an ethylene-acrylic acid alkyl ester copolymer, an ethylene-methacrylic acid alkyl ester copolymer, maleic acid-modified polyethylene, or maleic acid modified polypropylene; a polyamide resin such as nylon-6, nylon-6,6, nylon-6,10, or nylon-6,12; an aromatic polyester resin such as polyethylene terephthalate or a copolymer thereof, polyethylene naphthalate, or polybutylene terephthalate; a thermoplastic polyester resin such as an aliphatic polyester resin including polyvinyl acetate, polybutylene succinate, polylactic acid, or a poly(3-hydroxybutyrate/3-hydroxyvalerate) copolymer (PHBV); an acrylic resin such as poly(meth)acrylic acid (ester) or polyacrylonitrile; a polycarbonate resin such as aromatic polycarbonate or aliphatic polycarbonate; a polystyrene resin such as atactic polystyrene, syndiotactic polystyrene, a acrylonitrile-styrene (AS) copolymer, or an acrylonitrile-butadiene-styrene (ABS) copolymer; a polyvinyl chloride resin such as polyvinyl chloride or polyvinylidene chloride; polyphenylene sulfide; a polyether resin such as polyether sulfone, polyether ketone, or polyether ether ketone; and various known thermoplastic resins such as polyvinyl alcohol, rosin, a cellulose acetate thermoplastic resin, a petroleum hydrocarbon resin, a coumarone indene resin, etc. A plurality of thermoplastic

resins may be used in combination. Furthermore, an elastomer component such as a styrene-butadiene copolymer, a styrene-isoprene copolymer, a styrene-butadiene-ethylene copolymer, a styrene-isoprene-ethylene copolymer, an acrylonitrile-butadiene copolymer, or a fluoroelastomer may be included.

[0036]

Incorporation of such a resin can variously change a physical property of the thermoplastic composition of the present invention. For example, incorporation of rosin can improve water resistance of the thermoplastic composition. Furthermore, incorporation of a biodegradable resin such as polylactic acid or PHBV can facilitate biodegradation when the thermoplastic composition is disposed of and contribute to environment aspects.

[0037]

From the viewpoint of making the most of a physical property and processability of the thermoplastic composition of the present invention, as well as texture resulting from cellulose, not incorporating the thermoplastic resin is also possible. Furthermore, when such a thermoplastic resin is incorporated, a content thereof is preferably about 5 to 120% by mass, further about 10 to 100% by mass, especially about 20 to 80% by mass relative to 100% by mass of a total of cellulose, a hydroxycarboxylic acid, and a sugar.

[0038]

In another preferred embodiment of the thermoplastic composition of the present invention different from the above-

described embodiment, cellulose is contained in an amount of 5 to 40% by mass, a hydroxycarboxylic acid is contained in an amount of 5 to 40% by mass, a sugar is contained in an amount of 3 to 25% by mass, and a resin or a filler is contained in an amount of 20 to 80% by mass; more preferably cellulose is contained in an amount of 10 to 35% by mass, a hydroxycarboxylic acid is contained in an amount of 10 to 35% by mass, a sugar is contained in an amount of 5 to 20% by mass, a resin or a filler is contained in an amount of 30 to 70% by mass; and further preferably cellulose is contained in an amount of 15 to 30% by mass, a hydroxycarboxylic acid is contained in an amount of 15 to 30% by mass, a sugar is contained in an amount of 7 to 15% by mass, a resin or a filler is contained in an amount of 35 to 60% by mass. Such a composition can result in a thermoplastic composition having, in particular, excellent texture, heat resistance, water resistance, or mechanical property.

[0039]

(Other additives)

Additives other than those above-described may be incorporated in the thermoplastic composition of the present invention, as desired. Examples thereof include, but are not limited to, a colorant, a lubricant, a coupling agent, a flow modifier (flow regulator), a crosslinking agent, a dispersing agent, an antioxidant, a UV absorber, a flame retardant, a stabilizer, an antistatic agent, a foaming agent, a plasticizer, starch, casein, etc. These additives may be used

alone or two or more thereof may be used in combination. Furthermore, the additives may be incorporated in the below-described kneading step or may be incorporated in raw materials in advance before the kneading step. For example, a coupling agent may be included by applying it on a surface of cellulose or an inorganic filler.

[0040]

Contents of the other additives in the thermoplastic composition of the present invention may be freely set in accordance with a target physical property or processability, but preferably each of the other additives is contained in an amount of about 0 to 10% by mass and especially about 0.05 to 5% by mass and a total of the other additives is contained in an amount of 20% by mass or less, for example, 0.05 to 20% by mass relative to 100% by mass of a total of cellulose, a hydroxycarboxylic acid, and a sugar.

[0041]

[Method for producing thermoplastic composition]

The thermoplastic composition of the present invention can be produced by mixing components. The method is not particularly limited. For example, three components, that is, cellulose, a hydroxycarboxylic acid, and sugar, as well as an additive such as an inorganic filler or other resin components may be kneaded simultaneously or two components of the three components may be kneaded in advance and then other components may be added thereto and kneaded together.

[0042]

Here, in order to improve molding processability of the thermoplastic composition or when the thermoplastic composition is produced in a small amount in a low-shear mixer, for example, it is preferred that a hydroxycarboxylic acid and a sugar be melt-kneaded and then cellulose be kneaded therewith. Since the hydroxycarboxylic acid and the sugar can form an eutectic mixture, when the above-described two components are mixed in advance, the subsequent mixing can be performed at a mild temperature and under a low shear condition, reducing an energy consumption amount and preventing an organic matter from degrading at a high temperature.

[0043]

The present invention also encompasses a method for producing a thermoplastic composition, the method including a first step of mixing a hydroxycarboxylic acid and a monosaccharide and/or a disaccharide at a temperature of 150 to 240°C; and a second step of mixing the mixture obtained in the first step with cellulose at a temperature of 150 to 240°C (hereinafter, this method may be referred to as "Production method-A"). For example, when a thermoplastic composition containing cellulose in about 0.05 to 20.0% by mass relative to a total amount of thermoplastic composition is produced, Production method-A is effectively used.

[0044]

A method for mixing components in the method of the present invention, for example, Production method-A is not

particularly limited. For example, a method in which the components are mixed in a common kneader such as an extruder, a kneader, a Banbury mixer, a planetary mixer, a Henschel mixer, or a heated roll, etc. at a temperature of 150 to 240°C, especially 160 to 200°C may be used, but is not limited thereto. In the case of a small batch, the components may be mixed in a flask with a stirrer as described below.

[0045]

However, when mixing is performed on more than a certain scale (not only in the below-described Production method-B, but also in Production method-A), an extruder, especially a twin-screw extruder is preferably used. The extruder can uniformly disperse components by the action of high shear force upon mixing and the first step and the second step can be performed in a single device by adding cellulose at an extrusion stage. Of course, the first step and the second step may be, for example, performed in separate devices at different times. Furthermore, the first step and the second step may be performed in a kneader and the resulting mixture may be further kneaded in an extruder and molded.

[0046]

In one embodiment of Production method-A of the present invention, for example, the first step and the second step are performed in a twin screw extruder or a kneader, and the resulting mixture is extruded by a single- or twin-screw extruder. Thus, the thermoplastic composition of the present invention may be extruded into, for example, a strand shape

and cut into a prism or cylinder shape having a size of, for example, about 2 to 5 mm square by a pelletizer, resulting in a thermoplastic composition having the above-described composition in a pellet form. The present invention also encompasses a method for producing a thermoplastic composition, the method further including a third step in which the mixture obtained in the second step is kneaded and molded in an extruder.

[0047]

The thermoplastic composition of the present invention may also be produced by kneading cellulose, a hydroxycarboxylic acid, and a sugar simultaneously (this method may be referred to as "Production method-B"). For example, when a thermoplastic composition containing cellulose in about 5 to 60% by mass relative to a total amount of the thermoplastic composition is produced, Production method-B is advantageously employed using a high-shear mixer. Here, the high-shear mixer is not particularly limited. For example, the mixer may be an extruder, a kneader, a Banbury mixer, etc. with an extruder, especially a twin screw extruder being preferred. Such a mixer can mix a hydroxycarboxylic acid and a sugar with a high shear force and thus form a deep eutectic solvent even in the presence of another component. Therefore, a step of mixing only the above-described two components in advance may be omitted.

[0048]

The present invention also encompasses a method for

producing a thermoplastic composition, the method including mixing cellulose, a hydroxycarboxylic acid, and a monosaccharide and/or a disaccharide in an extruder at a temperature of 150 to 240°C. Such Production method-B allows a thermoplastic composition with excellent heat resistance or mechanical property to be easily produced and enables utilization of more cellulose waste.

[0049]

The extruder to be used in Production method-B is not particularly limited. A twin screw extruder is preferably used, but is not limited thereto. Furthermore, any type of twin screw extruder may be used. A kneading or extruding condition is also not limited and may be a temperature of 150 to 240°C, particularly 160 to 230°C, and especially 170 to 210°C. Furthermore, a component such as an inorganic filler or a resin may be kneaded simultaneous with three components, that is, cellulose, a hydroxycarboxylic acid, and a sugar or may be kneaded with a mixture of the three components. For example, only the above three components or a portion of other components may be kneaded by Production method-B with an extruder and then the remaining components may be kneaded in a mixer such as an extruder or a kneader.

[0050]

In Production method-B, a kneaded product may be formed directly into a molded product by extrusion from an extruder or may be molded into a pellet form. Furthermore, the resulting mixture may be subjected to a step similar to the

third step in the above-described Production method-A. For example, the mixture obtained by Production method-B may be extruded by a single- or twin-screw extruder into a strand shape and cut into a prism or cylinder shape having a size of about 2 to 5 mm square by, for example, a pelletizer, resulting in a thermoplastic composition having the above-described composition in a pellet form.

[0051]

[Molded product]

The present invention further encompasses a thermoplastic pellet made of the above-described thermoplastic composition. The thermoplastic composition of the present invention has excellent moldability since it melts or solidifies generally at a temperature of 50 to 230°C, specifically, in the case where the content of cellulose is about 0.05 to 20.0% by mass, at a temperature of about 60 to 200°C, further about 70 to 150°C, especially about 70 to 100°C, and in the case where the content of cellulose is about 5 to 60% by mass, at a temperature of about 150 to 240°C, further about 160 to 230°C, especially about 170 to 210°C, as described above. Therefore, the thermoplastic pellet of the present invention is suitable as a thermoplastic polymer material.

[0052]

The thermoplastic composition of the present invention has a good thermoplasticity as described above and thus can be molded into various shapes. The present invention also encompasses a molded product made of the thermoplastic

composition. A shape or size of the molded product is not particularly limited, and the molded product may be any shape such as sheet, tube, strand, or any other shape for any purpose. A method for molding the composition is also not particularly limited, any molding method such as extrusion molding, injection molding, roll molding, transfer molding, or blow molding may be used. For example, the above-described thermoplastic pellet of the present invention may be molded into a desired shape using an extruder or an injection molding device or the thermoplastic composition may be extruded without pelletizing and molded into a sheet or tubular product. It is also possible to combine it with another material using calendar molding.

[0053]

Application of the thermoplastic composition of the present invention or the molded product is not particularly limited. For example, it may be used for a daily necessity such as a toy, a toothbrush, or a bath product; a housing for a home appliance; or a polymeric material for transportation equipment such as an automobile or a train. In particular, when a refined product such as kraft pulp is used as a cellulose material, it can be used for a medical or food application. Since cellulose, a hydroxycarboxylic acid, a monosaccharide, and a disaccharide are highly safe materials, the thermoplastic composition of the present invention made of these components is suitable for a medical or food application. The thermoplastic composition of the present

invention can also be considered a natural product-derived material on the basis of a concept different from a conventional biodegradable resin, and can be utilized as an additive to another material for the purpose of increasing a biomass content.

EXAMPLES

[0054]

The present invention will be more specifically described with reference to Examples. Note that, these Examples are described only for the purpose of illustrating certain aspects and embodiments in order to facilitate a better understanding of the concept and scope of the invention as disclosed herein and described in the appended claims, and the invention is not limited in any way to these Examples.

[0055]

[Example 1]

(First step/Production method-A)

A flask with a stirrer was charged with 100 g of lactic acid and 40 g of glucose and stirred at a temperature of 150 to 200°C for 30 min. The resulting mixture was liquid at room temperature and had become a 100% natural deep eutectic solvent.

[0056]

(Second step/Production method-A)

A flask with a stirrer was charged with 100 g of the mixture obtained in the first step and heated to 150 to 200°C.

Then, 0.5 g of pulp was added thereto and stirred at about 150 to 200°C for 1 hour or longer, resulting in a nearly homogeneous brown liquid. The heating and the stirring at the above-described temperature were performed for a total of 8 hours. Then, once the liquid was transferred onto a clean aluminum plate, it solidified into a solid.

[0057]

(Property of composition)

The solid obtained in the second step had a resin-like appearance and feel. When the solid was hammered by a clean hammer, it became powdery. The resulting powder melted at a temperature of about 150°C and solidified again when cooled to near room temperature. Furthermore, the powder was able to be molded into a dumbbell specimen by injection molding. In other words, the composition obtained in this Example was demonstrated to be thermoplastic.

[0058]

Note that, when a simple experiment similar to in Example 1 was performed using another deep eutectic solvent instead of lactic acid and glucose in the first step, pulp was not uniformly microdispersed in the second step and did not exhibit thermoplasticity (see, Comparative Example 1). Although it is not possible to say for certain because of the simple experiment without precise temperature control during mixing, it is suggested that a thermoplastic material like the thermoplastic material of the present invention cannot be obtained merely by heating and mixing cellulose with a deep

eutectic solvent.

[0059]

[Example 2]

The powder obtained in Example 1 (thermoplastic composition) and starch were put into a small twin screw extruder at a mass ratio of 7:3 and kneaded and extruded at 80 to 120°C into a pellet. The resulting pellet was able to be molded into a dumbbell specimen by injection molding, as in Example 1.

[0060]

[Example 3]

The powder obtained in Example 1 (thermoplastic composition) and talc were put into a small twin screw extruder at a mass ratio of 6:4, and a pellet was produced in the same manner as in Example 2. The resulting pellet was able to be molded into a dumbbell specimen by injection molding, as in Examples 1 and 2.

[0061]

[Example 4]

The pellet obtained in Example 2 and poly(3-hydroxybutyrate/3-hydroxyvalerate) (PHBV, biodegradable resin) were put into a small twin screw extruder at a mass ratio of 1:1, and a pellet was produced in the same manner as in Example 2. The resulting pellet was able to be molded into a dumbbell specimen by injection molding, as in Examples 1 to 3.

[0062]

[Example 5]

The pellet obtained in Example 3 and gum rosin were put into a small twin screw extruder at a mass ratio of 8:2, and a pellet was produced in the same manner as in Example 3. The resulting pellet was able to be molded into a dumbbell specimen by injection molding, as in Examples 1 to 4.

[0063]

[Example 6]

A pellet was produced in the same manner as in Example 5, except that lignin (Vanillex (registered trademark) CN manufactured by Nippon Paper Industries Co., Ltd.) was used instead of gum rosin. The resulting pellet was able to be molded into a dumbbell specimen by injection molding, as in Examples 1 to 5.

[0064]

[Example 7]

A twin screw extruder (twin screw kneader extruder, manufactured by TECHNOVEL CORPORATION, ϕ 15mm, L/D = 50) was charged with 40 parts by mass of cedar wood flour, 50 parts by mass of lactic acid, 25 parts by mass of glucose, and 50 parts by mass of talc and extruded in a strand shape with kneading at a set temperature of 160 to 220°C (to thereby prepare a thermoplastic composition as described in Production method-B). Then, the strand was cut with a pelletizer to thereby form a pellet of the thermoplastic composition.

[0065]

Then, the resulting pellet was injection molded by an injection molding device (HAAKE Process 11 manufactured by

Thermo Fisher Scientific, Inc.) and was able to be molded into a specimen for a bending test according to JIS K7171 (ISO178) (80 x 10 x 4mm) and a dumbbell specimen for a tensile test according to JIS K7161-2 at 180 to 220°C. It was revealed that the composition of the present example was thermoplastic and exhibited a good molding processability although it contained a large amount of a cellulose component.

[0066]

Next, three of each of these specimens were subjected to a bending test according to JIS K7171 (test speed: 2 mm/min) and a tensile test according to JIS K7161-2 (tensile speed: 5 mm/min) to evaluate their mechanical strength. Furthermore, water resistance was also evaluated. Note that, water resistance was evaluated by adding the resulting thermoplastic resin pellet and the dumbbell specimen to a glass beaker containing water, visually observing for change in shape, and grading based on the following criteria.

(Evaluation criteria of water resistance)

Good (indicated by circle symbol (o)): No change in shape was observed. Fair (indicated by triangle symbol (Δ)): Specimen was changed in shape, but was not broken down. Poor (indicated by cross symbol (x)): Specimen was broken down in water and its shape was not retained. Evaluation results are shown in Table 1 below along with compositions of the thermoplastic compositions.

[0067]

[Examples 8 to 13]

Rosin or PHBV was used along with the components used in Example 7, and the same operations were performed as in Example 7. The composition of each of the thermoplastic compositions and evaluation results are shown in Table 1.

[0068]

[Table 1 Composition and evaluation result of samples]

Example		Exam- ple 7	Exam- ple 8	Exam- ple 9	Exam- ple 10	Exam- ple 11	Exam- ple 12	Exam- ple 13
*Compo- sition of sample	Ceder wood flour	40	50	50	50	50	50	50
	Lactic acid	50	50	50	50	50	50	50
	Glucose	25	25	25	25	25	25	25
	Talc	50	50	50	50	50	50	50
	Rosin	-	25	50	75	-	-	-
	PHBV	-	-	-	-	25	50	75
Cellulose amount*		24.2 (35)	25.0 (40)	22.2 (40)	20.0 (40)	25.0 (40)	22.2 (40)	20.0 (40)
Evalu- ation result	Tensile strength#	3.1	9.8	11.2	13.9	7.2	10.6	13.1
	Bending strength#	2.3	13.8	14.9	16.1	8.9	9.1	11.2
	Water resistance	Δ	O	O	O	O	O	O

* Unit: Part(s) by mass

× Unit: % by mass (Number within parentheses denotes % by mass relative to a total of three components, cellulose, lactic acid, and glycol)

Unit: MPa

[0069]

The above examples show that the compositions of the present invention each containing cellulose and an eutectic mixture of a hydroxycarboxylic acid and a sugar exhibit thermoplasticity and can be thermally melted and kneaded with various materials to provide various thermoplastic resin-like materials. In view of the fact that simply mixing cellulose

with a deep eutectic solvent did not result in a thermoplastic material (Comparative Example 1), the present invention is considered to be a thermoplastic material that exhibits an unexpected property.

[0070]

[Examples 14 to 19]

Polypropylene (PP) or polyethylene (PE) was used instead of rosin or PHBV, and the same operations were performed as in Examples 8 to 13. The composition of each of the thermoplastic compositions and evaluation results are shown in Table 2.

[0071]

[Table 2 Composition and evaluation result of samples]

Example		Exam- ple 7	Exam- ple 14	Exam- ple 15	Exam- ple 16	Exam- ple 17	Exam- ple 18	Exam- ple 19
*Compo- sition of sample	Ceder wood flour	40	50	50	50	50	50	50
	Lactic acid	50	50	50	50	50	50	50
	Glucose	25	25	25	25	25	25	25
	Talc	50	50	50	50	50	50	50
	PP	-	25	50	75	-	-	-
	PE	-	-	-	-	25	50	75
Cellulose amount*		24.2 (35)	25.0 (40)	22.2 (40)	20.0 (40)	25.0 (40)	22.2 (40)	20.0 (40)
Evalu- ation result	Tensile strength#	3.1	10.8	13.8	15.7	7.5	8.1	9.6
	Bending strength#	2.3	8.4	10.1	13.9	6.3	7.2	8.8
	Water resistance	Δ	○	○	○	○	○	○

* Unit: Part(s) by mass

× Unit: % by mass (Number within parentheses denotes % by mass relative to a total of three components, cellulose, lactic acid, and glycol)

Unit: MPa

[0072]

It is shown that the thermoplastic composition of the present invention can also contain a general-purpose resin such as polypropylene or polyethylene and thus improve a physical property such as a mechanical property or water resistance. Thus, the thermoplastic composition of the present invention can include a large amount of various resins or an inorganic filler and thus improve a physical property such as water resistance or reduce cost. For example, it was confirmed that up to 175 parts by mass of rosin was able to be incorporated to increase water resistance as in Examples 8 to 10.

[0073]

As described above, the thermoplastic composition of the present invention exhibits thermoplastic even when a large amount of cellulose is contained and useful for a recycling application of cellulose waste. The thermoplastic composition of the present invention can also be mixed with a petroleum-based resin including polyethylene to increase a biomass content. The thermoplastic composition of the present invention can also be mixed with a biodegradable resin including PHBV to increase a waste utilization rate without reducing a physical property, as well as to reduce a cost. In other words, the thermoplastic composition of the present invention can be used like a bulking agent. In addition, the thermoplastic composition of the present invention does not require disposal of a solvent or use of an environmentally

hazardous substance such as a halide-containing substance in a manufacturing process. Considering such points, the effect of this invention is remarkable.

CLAIMS

1. A thermoplastic composition comprising:
cellulose; and
an eutectic mixture of a monosaccharide and/or a disaccharide and a hydroxycarboxylic acid.
2. The thermoplastic composition according to claim 1, wherein the eutectic mixture is a mixture of lactic acid and glucose.
3. The thermoplastic composition according to claim 1 or 2, further comprising hemicellulose and/or lignin, wherein the cellulose is plant-derived cellulose.
4. The thermoplastic composition according to claim 1 or 2, wherein the composition comprises 0.05 to 60.0% by mass of the cellulose.
5. The thermoplastic composition according to claim 1 or 2, wherein the composition has a mass ratio of the hydroxycarboxylic acid : the monosaccharide and/or the disaccharide in a range of 1:2 to 6:1.
6. The thermoplastic composition according to claim 1 or 2, further comprising one or more substances selected from the group consisting of an inorganic filler, a natural

thermoplastic resin, a synthetic thermoplastic resin, and a biodegradable resin.

7. A method for producing a thermoplastic composition, the method comprising:

a first step of mixing a hydroxycarboxylic acid and a monosaccharide and/or a disaccharide at a temperature of 150 to 240°C; and

a second step of mixing the mixture obtained in the first step and cellulose at a temperature of 150 to 240°C.

8. The method for producing a thermoplastic composition according to claim 7, further comprising a third step of kneading and molding the mixture obtained in the second step in an extruder.

9. A method for producing a thermoplastic composition, the method comprising

mixing cellulose, a hydroxycarboxylic acid, and a monosaccharide and/or a disaccharide in an extruder at a temperature of 150 to 240°C.

10. A thermoplastic pellet formed of the thermoplastic composition according to claim 1 or 2.

11. A molded product formed of the thermoplastic composition according to claim 1 or 2.