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(54) **Title:** RESIN COMPOSITION AND ITS FILM

(57) **Abstract:** There are provided a biodegradable resin composition comprising a composition (A) comprising starch (a1), a condensation polymer (a2) of an aliphatic diol and an aliphatic dicarboxylic acid, and a condensation polymer (a3) of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid; and a composition (B) being at least one of an amorphous polylactic acid polymer (b1) and an aliphatic aromatic polyester (b2), wherein a mass ratio [(a1)/{(a2) + (a3)}] is in the range of 0.25 to 2.20, and a mass ratio [(A)/(B)] is in the range of 1 to 35, the biodegradable resin composition having improved moldability and improved mechanical characteristics such as tear strength and impact strength, as well as excellent bag-making suitability such as heat seal characteristics, and excellent economy, and also having a moderate biodegradation rate; and a biodegradable film using this biodegradable resin composition.



DESCRIPTION

Title of Invention

RESIN COMPOSITION AND ITS FILM

Technical Field

[0001]

The present invention relates to a biodegradable resin composition and a biodegradable film using the same. More particularly, the present invention relates to a biodegradable resin composition having improved moldability and improved mechanical characteristics such as tear strength and impact strength, as well as excellent bag-making suitability such as heat seal characteristics, and excellent economy, and also having a moderate biodegradation rate, and a biodegradable film using the above biodegradable resin composition preferred for compost bags, agricultural films, packaging materials, and the like.

Background Art

[0002]

It is known that biodegradable resins decompose relatively easily without producing harmful materials in water and in soil. Therefore, in terms of environmental conservation such as waste disposal problems, biodegradable resins attract attention worldwide. Among these, aliphatic polyester resins comprising aliphatic diols and aliphatic dicarboxylic acids have properties close to those of polyethylene, and therefore films obtained by molding these resins are promising as film applications such as agricultural materials, civil engineering materials,

vegetation materials, and packaging materials (for example, see Patent Literatures 1 and 2).

However, all conventional biodegradable films have insufficient tear strength, particularly in the machine (stretching) direction of the film, and have practical problems.

[0003]

On the other hand, the construction of a recycling-oriented society by conversion from depleted resources to renewable resources draws attention, and there is a growing interest in materials derived from natural products rather than materials synthesized from petroleum as raw materials. Examples of materials currently put to practical use as such materials derived from natural products include starch.

As starch to which moldability and properties for a film have been imparted, esterified vinyl ester-graft-polymerized starch (Patent Literature 3), a starch ester (Patent Literature 4), and further an alloy of polyester-graft-polymerized starch and a polyester (Patent Literature 5) are proposed. It is considered that when starch is further highly modified, the moldability and properties for a film can be further improved. But, this is not realistic in terms of cost.

In addition, combining a gelatinized product of starch and a thermoplastic resin is also proposed (for example, see Patent Literatures 6 and 7). Further, various propositions are also made for systems to which processed starch is added (for example, see Patent Literatures 8 to 11).

But, all these compositions have insufficient fluidity during heating and melting. Therefore, it is possible to some extent to obtain a molded material having a simple shape, for example, a thick sheet, by extrusion

molding, but when an attempt is made to mold an article having a complicated shape by injection molding, a molded material having the desired shape may not be obtained due to poor fluidity. In addition, the molding of a thin film by an inflation method is also difficult. Even if a thin film can be molded, the film properties are not practical. Another problem is that the starch gelatinization step and the blending step are separately needed, and the production cost increases.

As a method for solving these problems, a composition of oxidatively treated gelatinized starch and a biodegradable resin is proposed (Patent Literature 12). This is a method involving simultaneously performing gelatinization and oxidation. But problems are that it is difficult to control the decomposition of starch with an oxidant in the coexistence of water for gelatinization and a plasticizer and to sufficiently blend the above water, plasticizer, oxidant, and resin, and virtually the production cost increases. In other words, when gelatinization, oxidation, and compounding are simultaneously performed, the molecular weight of the biodegradable resin also decreases, and it is difficult to improve film moldability, and properties.

[0004]

When oxidatively treated gelatinized starch pellets and biodegradable resin pellets are molded by dry blending during molding as illustrated, no problem may occur in injection molding. But in thin film molding, kneading such pellets is insufficient with a melt extruder in inflation film molding usually used, and therefore problems with moldability and properties occur. In addition, the oxidant used in Patent Literature 12 is a peroxide, and the compatibility of the gelatinized starch with the biodegradable resin is insufficient. Therefore the moldability

when the resin composition is processed into a film is not sufficiently improved.

Patent Literatures 13 to 15 disclose resin compositions comprising oxidized starch and biodegradable resins and having improved moldability and mechanical characteristics, and further disclose adding additives and aliphatic aromatic polyesters to the resin compositions. But, in any of the methods, the film moldability and heat seal characteristics when a lactic acid polymer having a high melting point is added are not improved. In addition, by using an amorphous polylactic acid polymer, the moldability and heat seal properties are improved, but decreases in tear strength and impact strength are also not improved.

Citation List

Patent Literature

[0005]

PTL1: JP H5-271377 A

PTL2: JP H6-170941 A

PTL3: JP H8-239402 A

PTL4: JP 2939586 B

PTL5: JP H9-31308 A

PTL6: JP H1-217002 A

PTL7: JP H2-14228 A

PTL8: JP H3-56543 A

PTL9: JP H3-70752 A

PTL10: JP H3-74445 A

PTL11: JP H3-74446 A

PTL12: JP 3078478 B

PTL13: JP 2007-277353 A

PTL14: JP 2008-013602 A

PTL15: JP 2008-024764 A

Summary of Invention

Technical Problem

[0006]

The present invention has been made in view of the problems of the conventional art described above and provides a biodegradable resin composition having improved moldability and improved mechanical characteristics such as tear strength and impact strength, as well as excellent bag-making suitability such as heat seal characteristics, and excellent economy, and also having a moderate biodegradation rate, and a biodegradable film using this biodegradable resin composition.

Solution to Problem

[0007]

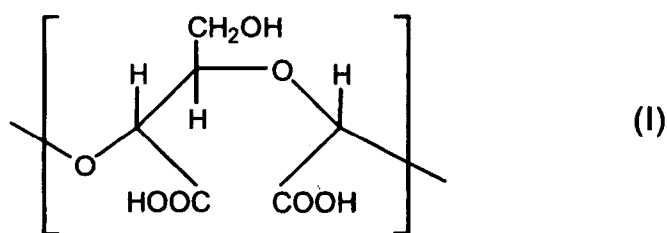
The present inventors have studied diligently in order to solve the above problems, and as a result found that the above problems can be solved by using a composition comprising starch, a condensation polymer of an aliphatic diol and an aliphatic dicarboxylic acid, a condensation polymer of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid, and at least one of an amorphous polylactic acid polymer and an aliphatic aromatic polyester, leading to the completion of the present invention.

Specifically, the gist of the present invention is the following [1] to [14].

[1] A biodegradable resin composition comprising a composition (A) comprising starch (a1), a condensation polymer (a2) of an aliphatic diol and an aliphatic dicarboxylic acid, and a condensation polymer (a3) of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid; and a composition (B) being at least one of an amorphous polylactic acid polymer (b1) and an aliphatic aromatic polyester (b2), wherein a mass ratio $[(a1)/\{(a2) + (a3)\}]$ is in the range of 0.25 to 2.20, and a mass ratio $[(A)/(B)]$ is in the range of 1 to 35.

[2] The biodegradable resin composition according to the [1], wherein the starch (a1) is oxidized starch having a repeating structure represented by the following general formula (I):

[0008]



[0009]

[3] The biodegradable resin composition according to the [1] or [2], wherein the starch (a1) is oxidized starch produced using sodium hypochlorite.

[4] The biodegradable resin composition according to any of the [1] to [3], wherein a mass ratio of the condensation polymer (a2) to the condensation polymer, (a3) $[(a2)/(a3)]$, is in the range of 0.5 to 12.

[5] The biodegradable resin composition according to any of the [1] to [4], wherein a mass ratio of the aliphatic diol to the tri- to hexa-functional aliphatic alcohol, [the aliphatic diol/the tri- to hexa-functional aliphatic alcohol], in the condensation polymer (a3) is in the range of 4 to 200.

[0010]

[6] The biodegradable resin composition according to any of the [1] to [5], wherein in the condensation polymer (a2), the aliphatic diol is one or more selected from ethylene glycol and 1,4-butanediol, and the aliphatic dicarboxylic acid is one or more selected from succinic acid and adipic acid.

[7] The biodegradable resin composition according to any of the [1] to [6], wherein in the condensation polymer (a3), the aliphatic diol is one or more selected from ethylene glycol and 1,4-butanediol, the aliphatic dicarboxylic acid is one or more selected from succinic acid and adipic acid, and the tri- to hexa-functional aliphatic alcohol is trimethylolpropane.

[0011]

[8] The biodegradable resin composition according to any of the [1] to [7], wherein the amorphous polylactic acid polymer (b1) is a polymer of L-lactic acid and D-lactic acid, and a content of the L-lactic acid and a content of the D-lactic acid are each 94 mol % or less.

[9] The biodegradable resin composition according to any of the [1] to [8], wherein the aliphatic aromatic polyester (b2) is one or more selected from a condensation polymer of an aliphatic polyol and an aromatic polycarboxylic acid, and a condensation polymer of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polycarboxylic acid.

[0012]

[10] The biodegradable resin composition according to any of the [1] to [9], wherein the composition (A) further comprises a solvent having a boiling point of 180°C or more.

[0013]

[11] The biodegradable resin composition according to any of the [1] to [10], wherein the composition (A) further comprises a plasticizer.

[12] The biodegradable resin composition according to the [11], wherein the plasticizer is one or more selected from polyglycerin acetate, a derivative thereof, and an adipic acid diester.

[0014]

[13] The biodegradable resin composition according to any of the [1] to [12], wherein the composition (A) comprises a composition obtained by melting and kneading by an extruder with a vent.

[14] A biodegradable film using the biodegradable resin composition according to any of the [1] to [13].

Advantageous Effects of Invention

[0015]

The present invention can provide a biodegradable resin composition having improved moldability and improved mechanical characteristics such as tear strength and impact strength, as well as excellent bag-making suitability such as heat seal characteristics, and excellent economy, and also having a moderate biodegradation rate, and a biodegradable film using this biodegradable resin composition.

The biodegradable film of the present invention has strong mechanical characteristics, particularly strong tear strength in the machine (stretching) direction, is preferred for compost bags, agricultural films, packaging materials, and the like, and also has excellent economy and flexibility.

Description of Embodiments

[0016]

[Biodegradable Resin Composition]

The biodegradable resin composition of the present invention is a biodegradable resin composition comprising a composition (A) comprising starch (a1), a condensation polymer (a2) of an aliphatic diol and an aliphatic dicarboxylic acid, and a condensation polymer (a3) of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid; and a composition (B) being at least one of an amorphous polylactic acid polymer (b1) and an aliphatic aromatic polyester (b2), wherein

the mass ratio $[(a1)/\{(a2) + (a3)\}]$ is in the range of 0.25 to 2.20, and the mass ratio $[(A)/(B)]$ is in the range of 1 to 35.

The biodegradable resin composition of the present invention will be described in detail below.

The condensation polymer (a2) of an aliphatic diol and an aliphatic dicarboxylic acid is hereinafter sometimes referred to as the "condensation polymer (a2)", and the condensation polymer (a3) of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid is hereinafter sometimes referred to as the "condensation polymer (a3)."

[0017]

<Composition (A)>

[Starch (a1)]

The starch (a1) that can be used in the present invention is not particularly limited. Examples thereof can include unprocessed starch such as potato starch, cornstarch, sweet potato starch, tapioca starch, sago palm starch, rice starch, and wheat starch, and processed starch

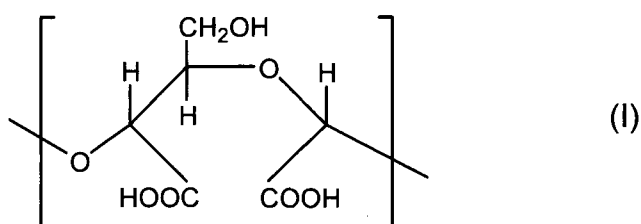
such as various types of esterified starch, etherified starch, and oxidized starch. Among these, oxidized starch is preferred, and especially oxidized starch having a repeating structure represented by the following general formula (I) is preferred. As the oxidized starch, a gelatinized product of oxidized starch produced using sodium hypochlorite is further preferred.

By using a gelatinized product of oxidized starch as the starch (a1), the moldability when the biodegradable resin composition is molded into a film is better, and the properties of the obtained biodegradable film improve.

[0018]

As the pretreatment for obtaining a gelatinized product of oxidized starch, first, treatment for forming the repeating structure represented by the following general formula (I), that is, breaking the bond between C-2 and C-3 carbons in some glucose units in starch and forming a carboxyl group on each of the C-2 and C-3 carbons, is performed.

[0019]



[0020]

Examples of the method for converting the glucose unit in starch into the structure represented by the above general formula (I) can include a method of oxidizing starch with sodium hypochlorite, a hypochlorite, a bleaching powder, hydrogen peroxide, potassium permanganate, ozone, or the like.

When starch is oxidatively treated with an oxidant such as a peroxide, depolymerization due to the breaking of C-C bonds and glycoside bonds occurs, and the breaking of the bonds between C-2 and C-3 carbons is not sufficient. As a result, the amount of carboxyl groups formed may be insufficient.

[0021]

The oxidation of starch with sodium hypochlorite or the like can be performed, for example, by adjusting a water suspension having a starch concentration of about 40 to 50% by mass, preferably about 45% by mass, at a pH of about 8 to 11, adding a sodium hypochlorite aqueous solution having a chlorine concentration of 8 to 12% by mass, preferably about 10% by mass, to this water suspension, and reacting the mixture at about 40 to 50°C for about 1 to 2 hours. The reaction is preferably performed with stirring in a corrosion-resistant reaction container under normal pressure. After the completion of the reaction, the target material is obtained by separation using a centrifugal dehydrator or the like, sufficient water washing, and drying.

[0022]

The amount of carboxyl groups in the starch (a1) can be expressed as a carboxyl group substitution degree (neutralization titration method), and it is preferably 0.001 to 0.100, more preferably 0.010 to 0.05, and further preferably 0.01 to 0.035.

As the oxidized starch, commercial oxidized starch can also be used. Examples thereof can include "Ace A" (high viscosity product) and "Ace C" (low viscosity product) manufactured by Oji Cornstarch Co., Ltd.

The method of oxidizing starch with sodium hypochlorite is described, for example, in "Denpun Kagaku no Jiten (Dictionary of Starch

Science" (Hidetsugu Fuwa, Asakura Publishing Co., Ltd., March 20, 2003, p. 408) and "Denpun Kagaku Handobukk (Starch Science Handbook)" (Jiro Nikuni, Asakura Publishing Co., Ltd., July 20 1977, p. 501).

[0023]

[Condensation Polymer (a2)]

The condensation polymer (a2) is not particularly limited as long as it is a resin comprising a condensation polymer of an aliphatic diol and an aliphatic dicarboxylic acid or an anhydride thereof as a component. From the viewpoint of moldability, the condensation polymer (a2) is preferably a thermoplastic condensation polymer.

The condensation polymer (a2) may be a resin belonging to any of chemically synthesized resins, microbial resins (resins produced by microbes), resins utilizing natural products, and the like. Examples thereof can include polybutylene succinate, polybutylene succinate-adipate, and polyethylene succinate. One of these may be used alone, or two or more of these may be used in combination.

In the present invention, from the viewpoint of film moldability, properties, and availability, chemically synthesized aliphatic polyesters are preferred. Further, from the viewpoint of obtaining a good molded article, those having a melting point of 50 to 180°C and a weight average molecular weight of 50,000 or more are preferred, and such aliphatic polyesters can be obtained by the dehydration polycondensation of polyols and aliphatic polycarboxylic acids.

The melting point of the condensation polymer (a2) is preferably 60 to 150°C, more preferably 75 to 100°C.

In addition, the weight average molecular weight of the condensation polymer (a2) is more preferably 150,000 or more, more preferably 190,000 or more, and further preferably 200,000 or more.

Further, the MFR (melt flow rate) of the condensation polymer (a2) is preferably 0.8 g/10 min or more, more preferably 1.0 g/10 min or more.

[0024]

The weight average molecular weight as used herein means a value measured with the following apparatuses and conditions.

GPC apparatus: Shodex (registered trademark) GPC SYSTEM-11

(manufactured by Showa Denko K.K.)

Eluent: CF₃COONa 5 mM/HFIP (hexafluoroisopropanol)

Sample columns: HFIP-800P and HFIP-80M × 2

Reference columns: HFIP-800R × 2

Polymer solution: 0.1 wt% HFIP sol., 200 μl

Column temperature: 40°C flow rate 1.0 ml/min

Pressure: 30 kg/cm²

Detector: Shodex RI

Molecular weight standard: PMMA (Shodex STANDARD M-75)

MFR (melt flow rate) measurement is performed at a temperature of 190°C and a load of 2.16 kg in accordance with JIS-K-7210.

[0025]

Examples of the aliphatic diol include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, decamethylene glycol, and neopentyl glycol.

Examples of the aliphatic dicarboxylic acid include succinic acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, and anhydrides thereof.

As the above condensation polymer (a2), those using at least one selected from ethylene glycol and 1,4-butanediol as the aliphatic diol, and using at least one selected from succinic acid and adipic acid as the aliphatic dicarboxylic acid are preferred.

The condensation polymer (a2) in the present invention may comprise, as other components other than the above, an oxycarboxylic acid, a polycarboxylic acid, and the like as copolymerization components. When the condensation polymer (a2) contains the above other components, their content is preferably 10% by mass or less, more preferably 5% by mass or less, in the condensation polymer (a2).

As commercial products of such a condensation polymer (a2), for example, "Bionolle (registered trademark)" series manufactured by Showa Denko K.K. is well-known and can be preferably used.

[0026]

[Condensation Polymer (a3)]

The condensation polymer (a3) is not particularly limited as long as it is a resin comprising a condensation polymer of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid or an anhydride thereof as a component. From the viewpoint of moldability, the condensation polymer (a) is preferably a thermoplastic condensation polymer.

Like the condensation polymer (a2), the condensation polymer (a3) may be a resin belonging to any of chemically synthesized resins, microbial resins (resins produced by microbes), resins utilizing natural products, and the like. One of these may be used alone, or two or more of these may be used in combination.

In addition, like the condensation polymer (a2), from the viewpoint of film moldability, properties, and availability, chemically synthesized aliphatic polyesters are preferred. Further, from the viewpoint of obtaining a good molded article, the melting point is preferably in the same range as the condensation polymer (a2).

The weight average molecular weight of the condensation polymer (a3) is preferably 50,000 or more, more preferably 80,000 or more, and further preferably 100,000 or more.

The MFR (melt flow rate) of the condensation polymer (a3) is preferably 5.0 g/10 min or more, more preferably 7.0 g/10 min or more.

The weight average molecular weight and the MFR are measured by the methods described for the condensation polymer (a2).

[0027]

As the aliphatic diol and the aliphatic dicarboxylic acid, the same compounds as the condensation polymer (a2) can be used.

Examples of the tri- to hexa-functional aliphatic alcohol include trimethylolpropane, pentaerythritol, glycerin, and a triallyl isocyanurate ethylene oxide adduct. In addition, examples of the tri- to hexa-functional aliphatic alcohol include glycidol, which is a monoepoxy compound in a dehydrated form.

As the above condensation polymer (a3), those using at least one selected from ethylene glycol and 1,4-butanediol as the aliphatic diol, using at least one selected from succinic acid and adipic acid as the aliphatic dicarboxylic acid, and using trimethylolpropane as the tri- to hexa-functional aliphatic alcohol are preferred.

[0028]

In the condensation polymer (a3), the mass ratio of the aliphatic diol to the tri- to hexa-functional aliphatic alcohol [the aliphatic diol/the tri- to hexa-functional aliphatic alcohol] is preferably in the range of 4 to 200, more preferably in the range of 4 to 180, and further preferably in the range of 4 to 150.

[0029]

[Mass Ratio between Starch (a1), Condensation Polymer (a2), and Condensation Polymer (a3)]

The mass ratio of the starch (a1) to the condensation polymer (a2) and the condensation polymer (a3), $[(a1)/\{(a2) + (a3)\}]$, is in the range of 0.25 to 2.20.

When the above mass ratio is less than 0.25, the balance between the production cost and the obtained effects, and the biodegradability deteriorate. When the above mass ratio exceeds 2.20, the properties of a biodegradable film obtained using the biodegradable resin composition decrease. In the present invention, the above mass ratio is in the range of 0.25 to 2.20, preferably in the range of 0.50 to 2.15, and more preferably in the range of 0.65 to 2.15.

[0030]

[Mass Ratio between Starch (a1) and Condensation Polymer (a2)]

The mass ratio of the starch (a1) to the condensation polymer (a2), $[(a1)/(a2)]$, is preferably in the range of 0.25 to 5. When the above mass ratio is 0.25 or more, the balance between the production cost and the obtained effects, and the biodegradability improve. When the above mass ratio is 5 or less, the properties of a biodegradable film obtained using the biodegradable resin composition improve. In the present

invention, the above mass ratio is more preferably in the range of 0.50 to 4, further preferably in the range of 0.65 to 3.5.

[0031]

[Mass Ratio between Condensation Polymer (a2) and Condensation Polymer (a3)]

The mass ratio of the condensation polymer (a2) to the condensation polymer (a3), [(a2)/(a3)], is preferably in the range of 0.5 to 12. When the above mass ratio is in the above range, the moldability, tear strength, and film properties improve. When the above mass ratio is less than 0.5, the moldability decreases. When the above mass ratio exceeds 12, the tear strength may decrease. In the present invention, the above mass ratio is more preferably in the range of 0.8 to 10, further preferably in the range of 1.0 to 9.5.

[0032]

The total of the starch (a1), the condensation polymer (a2), and the condensation polymer (a3) in the composition (A) is preferably 60 to 100% by mass, more preferably 65 to 100% by mass, and further preferably 70 to 100% by mass.

In addition to the starch (a1), the condensation polymer (a2), and the condensation polymer (a3), a crystalline polylactic acid polymer may be contained. The content when the crystalline polylactic acid polymer is contained is preferably 35% by mass or less, more preferably 30% by mass or less, and further preferably 25% by mass or less in the composition (A).

As used herein, a "polylactic acid polymer" refers to a polymer comprising 50 mol % or more of L-lactic acid and/or D-lactic acid as a structural unit. In addition, the "crystalline polylactic acid polymer"

refers to a polylactic acid polymer that has a melting point peak at 130°C or more when measurement is performed by a DSC comprising melting at 190°C followed by temperature decrease at 10°C/min to 20°C, and then scanning while increasing the temperature at 10°C/min.

[0033]

[Solvent]

The composition (A) in the present invention may comprise a solvent such as water as needed. The solvent other than water is not particularly limited, but solvents having polarity and having a boiling point of 180°C or more are preferred. The "boiling point" as used herein means a boiling point at 1 atmosphere.

Examples of the above polar solvents having a boiling point of 180°C or more can include ethylene glycol, propylene glycol, glycerin, sorbitol, polyethylene glycol, and polypropylene glycol. Especially, glycerin is preferably used from the viewpoint of the balance between the compatibility of the starch and the condensation polymer (a2) with the condensation polymer (a3), gelatinization ability, and cost. One of the above solvent such as water may be used alone, or two or more of the above solvents such as water may be used in combination.

[0034]

When the above solvent such as water is used, the amount of the solvent used in the composition (A) is preferably 2 to 20% by mass, more preferably 2 to 18% by mass, and further preferably 2 to 13% by mass. When two or more solvents are used, the total amount is preferably in the above range. By setting the amount of the solvent used in the above range, kneading becomes easy, and the deterioration of mechanical properties and moldability can be suppressed.

[0035]

[Plasticizer]

In the present invention, considering that the biodegradable resin composition is molded into a film, a plasticizer may be added to the composition (A). Particularly, when the composition (A) further comprises a polylactic acid polymer, a plasticizer is preferably added because mechanical properties such as tear strength and shock resistance improve.

As the above plasticizer, glycerin derivatives are preferred, and particularly polyglycerin acetate and derivatives thereof, adipic acid diesters, and the like are preferred.

The content of the plasticizer in the composition (A) is preferably 1 to 10% by mass, more preferably 2 to 8% by mass, and further preferably 2.5 to 5% by mass. When two or more plasticizers are used, the total amount is preferably in the above range. By setting the amount of the plasticizer added at 1% by mass or more, the film properties, particularly tensile elongation and film impact strength, are improved. By setting the amount of the plasticizer added at 10% by mass or less, the plasticizer can be prevented from bleeding to cause poor appearance.

[0036]

[Method for Producing Composition (A)]

As the method for producing the composition (A) in the biodegradable resin composition of the present invention, generally a method involving using an extruder used when a thermoplastic resin is melted and mixed, specifically a method comprising melting and kneading by an extruder with a vent, is preferred.

As a preferred embodiment in the present invention, one example of a method of preparing the composition (A) by simultaneously performing the gelatinization of the starch (a1) and the melting and mixing of the gelatinized product of the starch (a1), the condensation polymer (a2), and the condensation polymer (a3) will be described below.

First, as the apparatus, an extruder that is a twin screw type and is equipped with a vent for dehydration is preferably used in order to simultaneously perform the gelatinization and dehydration of the starch (a1) and the melting and mixing of the starch (a1) gelatinized, the condensation polymer (a2), and the condensation polymer (a3).

In addition, in order to ensure a sufficient amount of production, screw L/D is an important factor. The screw L/D is preferably 32 or more. As used herein, the "screw L/D" means the ratio of the effective length (L) of a screw to the diameter (D) of the screw.

Examples of an efficient method of dehydration and mixing is as follows: in the first step of performing the melting of the condensation polymer (a2) and (a3) and the gelatinization of starch, at the completion of the gelatinization of starch by heating and mixing, gas, water, and the like are removed by an open type vent to prevent backflow due to pressure increase in the extruder, and further in the second step of performing the mixing of the condensation polymer (a2) and (a3) and the gelatinized starch and the removal of water, dehydration is performed by a vacuum vent while the gelatinized product of starch, the condensation polymer (a2), and the condensation polymer (a3) are further mixed.

[0037]

In order to complete the above two steps by one extruder, it is essential that the screw L/D is 32 at the lowest. In an apparatus having

higher screw L/D, the amount of discharge can be increased, and therefore the production cost can be lowered.

In the above first step, the set temperature is preferably set at 60 to 150°C, more preferably 70 to 145°C, and further preferably 80 to 140°C in accordance with the softening temperature (or melting point) of the condensation polymer (a2). Many condensation polymers (a2) soften (melt) in the above temperature range, and therefore the mixing of the gelatinized starch, the condensation polymer (a2), and the condensation polymer (a3) can be performed in a molten state simultaneously with the gelatinization of starch.

[0038]

The residence time in the first step is preferably 30 to 180 seconds, more preferably 60 to 120 seconds, and further preferably 60 to 90 seconds. By setting the residence time at 30 seconds or more, the gelatinization of starch can be allowed to proceed sufficiently. By setting the residence time at 180 seconds or less, decomposition can be suppressed to ensure productivity.

In the second step, the set temperature is preferably set at 130 to 200°C, more preferably 140 to 190°C, and further preferably 150 to 180°C. By setting the set temperature in the above temperature range, the gelatinized product of starch, the condensation polymer (a2), and the condensation polymer (a3) are completely melted and mixed.

The residence time in the second step is preferably 30 to 120 seconds, more preferably 50 to 100 seconds, and further preferably 60 to 90 seconds. By setting the residence time at 30 seconds or more, the mixing of the gelatinized starch, the condensation polymer (a2), and the condensation polymer (a3) can be sufficiently performed. By setting the

residence time at 120 seconds or less, decomposition can be suppressed to ensure productivity.

[0039]

The composition (A) obtained in this manner is dried by setting to a temperature at which the condensation polymer (a2) and the condensation polymer (a3) do not soften (or melt), and heating in an oven under dry air for preferably 12 to 72 hours, more preferably 24 to 54 hours, and further preferably 36 to 48 hours.

The set temperature during drying is preferably 50 to 110°C, more preferably 60 to 100°C, and further preferably 70 to 90°C. The added water and the water contained in the starch at this stage are usually about 0.4% by mass or less. But, when water is contained, its content is not limited to this and can be 1.0% by mass or less in the composition (A) and is preferably 0.5% by mass or less, further preferably 0.3% by mass or less.

[0040]

<Composition (B)>

[Amorphous Polylactic Acid Polymer (b1)]

The amorphous polylactic acid polymer (b1) in the present invention refers to one that does not have a melting point peak at 130°C or more when measurement is performed by a DSC comprising melting at 190°C followed by temperature decrease at 10°C/min to 20°C, and scanning while increasing the temperature at 10°C/min. The amorphous polylactic acid polymer (b1) is not particularly limited as long as it satisfies this condition.

Examples of the amorphous polylactic acid polymer that satisfies such a condition include copolymers whose structural units are both L-lactic acid and D-lactic acid.

[0041]

As the polymerization method for the above amorphous polylactic acid polymer, known methods such as a polycondensation method and a ring-opening polymerization method can be adopted. For example, in the polycondensation method, a polylactic acid polymer having any composition can be obtained by direct dehydration polycondensation of a mixture of L-lactic acid and D-lactic acid.

In addition, in the ring-opening polymerization method, a polylactic acid polymer can be obtained with lactide, which is a cyclic dimer of lactic acid, using an appropriately selected catalyst while using a polymerization modifier and the like as needed. Lactide includes L-lactide, which is a dimer of L-lactic acid, D-lactide, which is a dimer of D-lactic acid, and further DL-lactide comprising L-lactic acid and D-lactic acid. By mixing these as needed and polymerizing these, an amorphous polylactic acid polymer having any composition can be obtained.

[0042]

In the present invention, a small amount of a copolymerization component can also be added according to the need to improve heat resistance, and the like. As the copolymerization component, non-aliphatic dicarboxylic acids such as terephthalic acid, non-aliphatic diols such as an ethylene oxide adduct of bisphenol A, and the like can be used. In addition, for the purpose of increasing molecular weight, a small amount of a chain extender, for example, a diisocyanate compound, an epoxy compound, or an acid anhydride, can also be used.

[0043]

The amorphous polylactic acid polymer in the present invention may be further a copolymer with another hydroxycarboxylic acid unit such as an α -hydroxycarboxylic acid, or a copolymer with one or more selected from an aliphatic diol and an aliphatic dicarboxylic acid.

Examples of the above another hydroxy-carboxylic acid unit include bifunctional aliphatic hydroxy-carboxylic acids such as glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxy-n-butyric acid, 2-hydroxy3,3-dimethylbutyric acid, 2-hydroxy3-methylbutyric acid, 2-methyl-lactic acid, and 2-hydroxycaproic acid, and lactones such as caprolactone, butyrolactone, and valerolactone.

In addition, examples of the aliphatic diol copolymerized into the above polylactic acid polymer include ethylene glycol, 1,4-butanediol, and 1,4-cyclohexanedimethanol. In addition, examples of the aliphatic dicarboxylic acid include succinic acid, adipic acid, suberic acid, sebacic acid, and dodecanedioic acid.

When the amorphous polylactic acid polymer (b1) contains the above small amount of the copolymerization component, the above small amount of the chain extender, or another hydroxycarboxylic acid unit, their total content is preferably 25 mol % or less in the amorphous polylactic acid polymer (b1).

[0044]

The weight average molecular weight of the amorphous polylactic acid polymer is preferably 60,000 to 700,000, more preferably 60,000 to 400,000, and further preferably 60,000 to 300,000. When the weight average molecular weight is in the above range, practical properties such as mechanical properties and heat resistance improve, and the melt

viscosity is not too high, and therefore the molding processability improves. The weight average molecular weight is measured by the method described for the condensation polymer (a2).

[0045]

The amorphous polylactic acid polymer in the present invention comprises L-lactic acid and D-lactic acid as repeating units, and the content of the L-lactic acid and the content of the D-lactic acid are each preferably 94 mol % or less, more preferably 92 mol % or less, and further preferably 90 mol % or less. When the content is in the above range, no crystallinity develops in the polylactic acid polymer, and therefore the dispersibility in the obtained biodegradable resin composition improves, and the moldability and the properties improve.

[0046]

The mass ratio of the composition (A) to the amorphous polylactic acid polymer (b1), $[(A)/(b1)]$, in the present invention is preferably in the range of 1 to 40. When the above mass ratio is 40 or less, the biodegradation rate is not too fast, and the properties (Young's modulus) of the film improve. On the other hand, when the above mass ratio is 1 or more, the production cost can be reduced, and a too slow biodegradation rate can be prevented. Further, the moldability when a biodegradable film is produced is good, and the tear strength and tensile break strength of the film improve. From such a viewpoint, the above mass ratio is more preferably in the range of 1 to 36, more preferably in the range of 1 to 34, and further preferably in the range of 1 to 32.

[0047]

[Aliphatic Aromatic Polyester (b2)]

The aliphatic aromatic polyester (b2) in the present invention is not particularly limited as long as it comprises a condensation polymer of an aliphatic polyol and an aromatic polycarboxylic acid, a condensation polymer of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polycarboxylic acid, a condensation polymer of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polyol, or a mixture of these condensation polymers.

As the aliphatic aromatic polyester (b2) in the present invention, thermoplastic aliphatic aromatic polyesters are preferably used from the viewpoint of moldability, and the aliphatic aromatic polyester (b2) is preferably one or more selected from a condensation polymer of an aliphatic polyol and an aromatic polycarboxylic acid, and a condensation polymer of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polycarboxylic acid.

[0048]

Examples of the aliphatic polyol include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, decamethylene glycol, and neopentyl glycol.

Examples of the aromatic polyol include hydroquinone, resorcin, catechol, and bisphenol A.

Examples of the aliphatic polycarboxylic acid include succinic acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, and anhydrides thereof.

Examples of the aromatic polycarboxylic acid include terephthalic acid, isophthalic acid, and anhydrides thereof.

[0049]

The aliphatic aromatic polyester in the present invention may be a resin belonging to any of chemically synthesized resins, microbial resins,

resins utilizing natural products, and the like. Examples thereof can include polybutylene succinate terephthalate, polybutylene adipate terephthalate, polybutylene succinate adipate terephthalate, polyethylene succinate terephthalate, and polyethylene adipate terephthalate. One of these may be used alone, or two or more of these may be used in combination.

Among these, polybutylene adipate terephthalate is preferred from the viewpoint of film moldability and film properties.

[0050]

Further, as the aliphatic aromatic polyester, those having a melting point of 50 to 180°C and a weight average molecular weight of 50,000 or more are preferred from the viewpoint of obtaining a good molded article. The weight average molecular weight is measured by the method described for the condensation polymer (a2).

Such an aliphatic aromatic polyester is usually obtained by the dehydration co-condensation of an aliphatic polyol and an aromatic polycarboxylic acid, or the dehydration co-condensation of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polycarboxylic acid.

The melting point is more preferably 70 to 160°C, further preferably 90 to 140°C.

The weight average molecular weight is more preferably 80,000 or more, further preferably 100,000 or more. The weight average molecular weight is measured by the method described for the condensation polymer (a2).

In addition, the aliphatic aromatic polyester in the present invention may be one obtained by copolymerizing a small amount of a

trifunctional or tetrafunctional polyol such as trimethylolpropane or pentaerythritol, an oxycarboxylic acid such as dimethylolpropionic acid, or a polycarboxylic acid such as butanetetracarboxylic acid or trimellitic acid as another component.

When the aliphatic aromatic polyester (b2) contains the above another component, its content is preferably 10% by mass or less, more preferably 5% by mass or less, in the aliphatic aromatic polyester (b2).

Examples of commercial products of the aliphatic aromatic polyester can include "Ecoflex (registered trademark)" manufactured by BASF.

[0051]

The method for mixing the above composition (A) and the composition (B) being at least one of the amorphous polylactic acid polymer (b1) and the aliphatic aromatic polyester (b2) is not particularly limited. Examples thereof can include a method comprising kneading with an extruder before molding usually performed with thermoplastic resins. From the viewpoint of cost, it is also possible to mix pellets of the respective components and mix them while melting them in a molding machine during molding. Kneading before molding is also possible, but from the viewpoint of cost, it is preferred to mix pellets of the components and mix them while melting them in a molding machine when molding.

For the mixing of the composition (A) and the composition (B), the composition (A) may be previously mixed with the amorphous polylactic acid polymer (b1), followed by adding the aliphatic aromatic polyester (b2) thereto, and alternatively, the amorphous polylactic acid polymer (b1) and the aliphatic aromatic polyester (b2) may be simultaneously added to the composition (A) and mixed. Thus, the order of mixing is not limited.

[0052]

In the present invention, mixing is preferably performed so that the mass ratio of the total of the composition (A) and the amorphous polylactic acid polymer (b1) to the aliphatic aromatic polyester (b2), $[(A) + (b1)]/(b2)$, is in the range of 1 to 70 from the viewpoint of moldability when a biodegradable film is produced, and the properties of the obtained biodegradable film. When the above mass ratio is in the above range, the film impact strength and the tear strength improve. From such a viewpoint, the above mass ratio is preferably in the range of 2 to 60, more preferably in the range of 2.5 to 50, and further preferably in the range of 3 to 20.

[0053]

In the present invention, the above composition (A) and the composition (B) are mixed so that the mass ratio $[(A)/(B)]$ is in the range of 1 to 35 from the viewpoint of moldability when the biodegradable resin composition is molded to produce a biodegradable film, and the properties of the obtained biodegradable film. When the above mass ratio is in the above range, the film impact strength and the tear strength improve. From such a viewpoint, the above mass ratio is in the range of 1 to 35, preferably in the range of 1 to 30, more preferably in the range of 3 to 25, and further preferably in the range of 5 to 20.

[0054]

[Biodegradable Film]

The biodegradable film of the present invention uses the biodegradable resin composition of the present invention described above, has a moderate biodegradation rate, and can be preferably used for compost bags, agricultural films, packaging materials, and the like.

The biodegradable film of the present invention can be continuously produced, for example, by melting and mixing a gelatinized product of starch and an aliphatic polyester using an extruder to prepare the composition (A), further injecting the composition (B) by a side feed to form a biodegradable resin composition, and then coupling the extruder outlet to a known water-cooling or air-cooling inflation molding or T-die film molding machine. The biodegradable film of the present invention may be produced by pelletizing or flaking the biodegradable resin composition and then molding the pellets or flakes using a known water-cooling or air-cooling inflation molding or T-die film extrusion molding machine.

[0055]

In addition, additives usually used in the art, for example, an antioxidant, a heat stabilizer, an ultraviolet inhibitor, an antistatic agent, a flame retardant, a crystallization promoter, and a filler, may be added to the biodegradable film of the present invention if needed, as long as that does not impair the characteristics of the present invention.

Specifically, examples of the antioxidant can include hindered phenol antioxidants such as p-t-butylhydroxytoluene and p-t-butylhydroxyanisole.

Examples of the heat stabilizer can include triphenyl phosphite and trisnonylphenyl phosphite.

Examples of the ultraviolet absorbing agent can include p-t-butylphenyl salicylate, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone, and 2,4,5-trihydroxybutyrophenone.

Examples of the antistatic agent can include N,N-bis(hydroxyethyl)alkylamines, alkylamines, alkylaryl sulfonates, and alkyl sulfonates.

Examples of the flame retardant can include hexabromocyclododecane, tris-(2,3-dichloropropyl) phosphate, and pentabromophenyl allyl ether.

Examples of the crystallization promoter can include talc, boron nitride, polyethylene terephthalate, and polytranscyclohexanedimethanol terephthalate.

Examples of the filler can include inorganic fillers such as clay, talc, and calcium carbonate, and organic fillers such as cellulose powders, cotton powders, and wood powders.

[0056]

When the production of the film is performed using the biodegradable resin composition pelletized or flaked once, rather than continuously performing the production of the film following the preparation of the biodegradable resin composition, as described above, the set temperature of the inflation molding or T-die film extrusion molding machine is the same as the above second step, that is, preferably about 130 to 180°C, more preferably 145 to 170°C, and further preferably 150 to 165°C.

The biodegradable film of the present invention may be one obtained by further uniaxially or biaxially stretching the above film.

In the biodegradable resin composition of the present invention, the moldability when it is molded into a biodegradable film is improved, and therefore the productivity is high, and in the obtained biodegradable film, the mechanical characteristics, particularly the impact strength of the

film, are improved, and therefore the biodegradable film is preferably used for compost bags, agricultural films, packaging materials, and the like having biodegradability. Further, the biodegradable resin composition and the biodegradable film have a moderate biodegradable rate and hydrolysis rate, and therefore a demand according to a use environment can be quickly addressed at low cost.

Examples

[0057]

The present invention will be further described below by giving Examples and Comparative Examples, but the present invention is not limited to the following examples in any way.

[Examples 1 to 18 and Comparative Examples 1 to 10]

A composition (A) comprising starch (a1), a condensation polymer (a2), and a condensation polymer (a3), and a composition (B) being one or more selected from an amorphous polylactic acid polymer (b1) and an aliphatic aromatic polyester (b2), and the like were blended as described in Tables 1 and 2, and a biodegradable film was fabricated according to the following procedure. The amounts blended and blending ratios in Tables 1 and 2 are expressed in parts by mass and mass ratios respectively.

[0058]

<Biodegradable Film Production Procedure>

The raw materials and additives other than the composition (B) were mixed by a super mixer and melted and kneaded using a corotating twin screw extruder (having a screw L/D of 42) equipped with a vent for dehydration and having a screw diameter of 65 mm to obtain pellets of

the composition (A). The set temperature is 80 to 140°C in the first step and 150 to 180°C in the second step. The residence time in the first step is 60 to 90 seconds, and the residence time in the second step is 60 to 90 seconds.

The pellets of the composition (A) were dried by a dehumidifying and air-circulating dryer at a temperature of 70°C for 48 hours. A dry blend of these pellets of the composition (A), pellets of the amorphous polylactic acid polymer (b1), and/or pellets of the aliphatic aromatic polyester (b2) were molded into a film having a thickness of 30 µm and a folded width of 300 mm (corresponding to blowup ratio = 3) by an inflation molding machine manufactured by Placo Co., Ltd. The molding temperature was 165°C.

The amount of water blended in Tables 1 and 2 is the amount of water added during the mixing of the components (A), and the content of water in the pellets after drying was about 0.3% by mass.

[0059]

<Raw Materials Used>

(1) Starch (a1-1)

Oxidized starch "Ace A" manufactured by Oji Cornstarch Co., Ltd.

Carboxyl group substitution degree: 0.01

Viscosity: 300 ± 50 BU

(Brabender viscosity, concentration 20% by mass, 50°C, measured after 1 hour)

"BU" is the viscosity unit of starch and can be measured using an Amylograph tester (manufactured by Brabender GmbH & Co. KG).

Water 12% by mass (normal pressure heating method 105°C, 4 hours)

(2) Starch (a1-2)

Cornstarch (raw starch) manufactured by Oji Cornstarch Co., Ltd.

Carboxyl group substitution degree: 0

Viscosity 1100 ± 50 BU

(Brabender viscosity, concentration 8% by mass, 50°C, measured after 1 hour)

Water 12% by mass (normal pressure heating method 105°C, 4 hours)

(3) Starch (a1-3)

Oxidized starch "Ace C" manufactured by Oji Cornstarch Co., Ltd.

Carboxyl group substitution degree 0.03

Viscosity 200 ± 50 BU

(Brabender viscosity, concentration 30% by mass, 50°C, measured after 1 hour)

Water 12% by mass (normal pressure heating method 105°C, 4 hours)

(4) Condensation polymer (a2-1)

Dehydration condensation type aliphatic polyester manufactured by Showa Denko K.K.

"Bionolle 5001MD" (melting point; 80°C, MFR; 1.2 g/10 min)

(The monomers are 1,4-butanediol, succinic acid, and adipic acid)

Weight average molecular weight: 200,000

(5) Condensation polymer (a2-2)

Dehydration condensation type aliphatic polyester manufactured by Showa Denko K.K.

"Bionolle 3001MD" (melting point; 95°C, MFR; 1.2 g/10 min)

(The monomers are 1,4-butanediol, succinic acid, and adipic acid)

Weight average molecular weight: 200,000

(6) Condensation polymer (a3-1)

Dehydration condensation type aliphatic polyester manufactured by Showa Denko K.K.

"Bionolle 1903MD" (melting point; 113°C, MFR; 8.1 g/10 min)

(The monomers are 1,4-butanediol, succinic acid, adipic acid, and trimethylolpropane)

Mass ratio [aliphatic diol/tri- to hexa-functional aliphatic alcohol]:
140

(7) Amorphous polylactic acid polymer (b1-1)

Polylactic acid polymer manufactured by NatureWorks LLC

Ingeo 4060D (melting point; none, MFR; 6.0 g/10 min)

L-lactic acid content 88 mol %, D-lactic acid content 12 mol %

Weight average molecular weight: about 120,000

(8) Crystalline polylactic acid polymer (x1-1)

Polylactic acid polymer manufactured by NatureWorks LLC

Ingeo 4032D (melting point; 160°C, MFR; 3.7 g/10 min)

L-lactic acid content 98.6 mol %, D-lactic acid content 1.4 mol %

(9) Crystalline polylactic acid polymer (x1-2)

Polylactic acid polymer manufactured by NatureWorks LLC

Ingeo 2002D (melting point; 150°C, MFR; 2.6 g/10 min)

L-lactic acid content 95.7 mol %, D-lactic acid content 4.3 mol %

(10) Aliphatic aromatic polyester (b2-1)

Dehydration condensation type aliphatic aromatic polyester manufactured by BASF

"Ecoflex" (melting point; 120°C, MFR; 4.0 g/10 min)

(The monomers are 1,4-butanediol, terephthalic acid, and adipic acid)

Weight average molecular weight: 120,000

(11) Water: deionized water

(12) Polar solvent: glycerin, boiling point: 290°C

(13) Plasticizer (p-1)

Polyglycerin acetate [RIKEMAL (registered trademark) PL-710]
manufactured by RIKEN VITAMIN Co., Ltd.

(14) Plasticizer (p-2)

Adipic acid diester [Adeka Cizer (registered trademark) RS-107]
manufactured by ADEKA CORPORATION
[0060]

The melting points of the above (4) to (10) were measured by a DSC (Differential Scanning Calorimeter) by melting at 190°C followed by temperature decrease at 10°C/min to 20°C followed by temperature increase at 10°C/min to melting peak temperature. Measurement was performed under the conditions of a temperature of 190°C and a load of 21.18 N in accordance with JIS K7210.

In addition, the L-isomer and D-isomer content of the polylactic acid polymer resin in the biodegradable resin composition was measured as follows.

0.3 g of the resin composition was weighed and added to 6 mL of a 1 N-potassium hydroxide/methanol solution, and the mixture was sufficiently stirred at 65°C. Then, 450 μ L of sulfuric acid was added, and the mixture was stirred at 65°C to decompose the polylactic acid polymer. 5 mL was measured as a sample. 3 mL of pure water and 13 mL of methylene chloride were mixed with this sample, and the mixture was

shaken. After standing and separation, about 1.5 mL of the lower organic layer was taken and filtered by a HPLC disk filter having a pore diameter of 0.45 μm followed by gas chromatography measurement using a HP-6890 Series GC system manufactured by Hewlett Packard. The proportion (%) of the peak area of methyl D-lactate ester in the total peak area of methyl lactate ester was calculated, and this was taken as the D isomer content (mol %) of the polylactic acid polymer resin. From this content, the L isomer content (mol %) was calculated.

[0061]

<Evaluation Methods>

(Inflation Film Moldability)

The evaluation was three-grade evaluation as follows.

Good: the bubble is stable, and a film having predetermined dimensions is obtained

Fair: the bubble is unstable, and a film having predetermined dimensions cannot be adjusted

Poor: no bubble forms or a blowout occurs, which results in a failure in molding

[0062]

(Tear Strength)

The tear strength (N) of a film measured according to JIS P-8116 using a pendulum Elmendorf tear tester (manufactured by TOYO SEIKI SEISAKUSYO CO., LTD.) was divided by film thickness (mm) to provide tear strength. Based on this, four-grade evaluation was performed.

Very Good: the tear strength is 100 N/mm or more

Good: the tear strength is 60 N/mm or more and less than 100 N/mm

Fair: the tear strength is 12 N/mm or more and less than 60 N/mm

Poor: the tear strength is less than 12 N/mm

[0063]

(Film Properties)

The film properties were evaluated by four grades based on the measurement results of the following tensile break strength, tensile break elongation, Young's modulus, impact strength, heat seal strength, and tear strength.

Very Good: a case where the film has a tensile break strength of 20 MPa or more, a tensile break elongation of 100% or more, a Young's modulus of 250 MPa or more, an impact strength of 30 kJ/m or more, a heat seal strength of 6 N/15 mm or more, and a tear strength of 12 N/mm or more

Good: a case where any one item of the above is not satisfied

Fair: a case where any two items of the above are not satisfied

Poor: a case where any three or more items of the above are not satisfied

All of the mechanical characteristics other than the impact strength and the heat seal strength were measured in both the longitudinal direction (film take-up direction, MD) and the transverse direction (TD). The heat seal strength was measured only in the longitudinal direction and determined using the value.

[0064]

Each measurement method is as follows.

- Tensile break strength: The tensile break strength was measured according to JIS Z-1702.
- Tensile break elongation: The tensile break elongation was measured according to JIS Z-1702.
- Young's modulus: The Young's modulus was measured according to ASTM D-822.

- Impact strength: The impact strength was measured according to JIS P-8134.
- Heat seal strength: The heat seal strength was measured according to JIS Z-0238.
- Tear strength: The tear strength was measured by the above-described method.

The above mechanical characteristics were measured for each film only when the film moldability was evaluated as Good or Fair and a film was obtained, and whether the above criteria were satisfied in both directions was determined.

[0065]

(Biodegradation Rate)

A film having a width of 30 mm, a length of 90 mm, and a thickness of 30 μm was buried in compost in a plastic container, and the plastic container was placed in an oven at 40°C for 10 days. Then, the amount of mass decrease was measured, and from the proportion of decrease, the biodegradation rate was evaluated by the following four grades considering performance demanded of agricultural mulch films and the like. When the biodegradation rate is significantly faster than the period of use of the film, problems such as the tearing and scattering of the film occur. When the biodegradation rate is significantly slow, a problem is that the film does not decompose and remains even if plowed in.

Very Good: the mass decrease rate is 10% or more and less than 30%

Good: the mass decrease rate is 30% or more and less than 60%

Fair: the mass decrease rate is 60% or more and less than 80%

Poor: the mass decrease rate is 80% or more and less than 100%

[0066]

(Hydrolysis Rate)

Each film sample was placed in a thermo-hygrostat at 60°C and 95% RH. After 1 week, a tensile test was carried out, and the retention rate with respect to initial properties (properties immediately after molding) was obtained for MD tensile break elongation. Based on this, evaluation by the following three grades was performed.

Good: the retention rate after 1 week is 80% or more

Fair: the retention rate after 1 week is 50% or more and less than 80%

Poor: the retention rate after 1 week is less than 50%

[0067]

(Crystallization Temperature)

For crystallization temperature, using a DSC apparatus ("DSC-200" manufactured by Rigaku Corporation), about 7 mg of a specimen was maintained in nitrogen at 200°C for 5 minutes, and then measurement was performed at a temperature decrease rate of 10°C/min, and the peak temperature was taken as the crystallization temperature.

[0068]

Table 1

Ex. No.	Composition (A)										Composition (B)		Biodegradable resin composition (numerical values are in mass ratios)					Tear strength	Film properties	Biodegradation rate	Hydrolysis rate	Crystallization temperature (°C)	Starch/polyester composition ratio						
	Innumerical values of amounts blended are in parts by mass			Polymer(x1)			Polymer(b1)		Polymer(b2)		Condensation polymer (A)	Polymer(b1)	Polymer(b2)	(A)/(b1)	(A)+(b1)/(b2)	(A)/(B)													
	Starch (a1)	Condensation polymer (a2)		Water	Polar solvent	Plasticizer		Polymer(x1)		Polymer(b1)							Polymer(b2)												
		Type	Amount			Type	Amount	Type	Amount														Type	Amount					
	Type	Amount	Type	Amount			Type	Amount	Type	Amount	Type											a1 /a2	a2 /a3	a1/ a2+a3					
Examples	1	a1-1	38	a2-1	45	a3-1	5	6	3	p-2	3	-	-	b2-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	60.4	0.84	9.00	0.76	
	2	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b2-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	73.4	0.86	4.20	0.69	
	3	a1-1	38	a2-1	45	a3-1	5	6	3	p-2	3	-	-	b1-1	b2-1	75	20	5	3.75	19.0	3.00	Good	Very Good	Good	59.5	0.84	9.00	0.76	
	4	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	75	20	5	3.75	19.0	3.00	Good	Very Good	Good	72.2	0.86	4.20	0.69	
	5	a1-1	38	a2-1	45	a3-1	5	6	3	p-2	3	-	-	-	b2-1	85	0	15	-	5.67	5.67	Good	Very Good	Good	62.9	0.84	9.00	0.76	
	6	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	-	b2-1	75	0	25	-	3.00	3.00	Good	Very Good	Good	73.3	0.86	4.20	0.69	
	7	a1-3	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	72.6	0.86	4.20	0.69	
	8	a1-1	36	a2-1	42	a3-1	10	6	3	p-1	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	75.7	0.86	4.20	0.69	
	9	a1-1	36	a2-2	42	a3-1	10	6	3	p-1	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	74.4	0.86	4.20	0.69	
	10	a1-1	50	a2-2	28	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	79.0	1.79	2.80	1.32	
	11	a1-1	60	a2-2	18	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Very Good	Good	84.6	3.33	1.80	2.14	
	12	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	95	3	2	31.7	49.0	19.0	Good	Good	Good	79.7	0.86	4.20	0.69	
	13	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	50	40	10	1.25	9.00	1.00	Good	Very Good	Good	66.3	0.86	4.20	0.69	
	14	a1-1	36	a2-1	31	a3-1	21	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Good	Good	80.4	1.16	1.48	0.69	
	15	a1-1	36	a2-1	26	a3-1	26	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Good	Good	81.3	1.38	1.00	0.69	
	16	a1-2	36	a2-1	42	a3-1	10	6	3	p-2	3	-	-	b1-1	b2-1	85	10	5	8.50	19.0	5.67	Good	Good	Good	78.5	0.86	4.20	0.69	
	17	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	x1-1	20	-	b2-1	95	-	5	-	19.0	19.0	19.0	Good	Very Good	Good	70.7	0.86	4.20	0.69
	18	a1-1	36	a2-1	42	a3-1	10	6	3	p-2	3	x1-1	20	-	b2-1	95	-	5	-	19.0	19.0	19.0	Good	Very Good	Good	71.2	0.86	4.20	0.69

Examples

[0069]

Table 2

Table 2	Composition (A)															Composition (B)		Biodegradable resin composition (numerical values are in mass ratios)					Film moldability	Tear strength	Film properties	Biodegradation rate	Hydrolysis rate	Crystallization temperature (°C)	Starch/polyester composition ratio		
	Numerical values of amounts blended are in parts by mass										Polymer(x1)		Composition (B)		Polymer(b1) Polymer(b2) (A)/(b1) (A)+(b1)/(b2) (A)/(B)																
	Starch (a1)		Condensation polymer (a2)		Condensation polymer (a3)		Water		Polar solvent		Plasticizer		Polymer(b1)		Polymer(b2)		Polymer(b1) Polymer(b2) (A)/(b1) (A)+(b1)/(b2) (A)/(B)														
	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Polymer(b1) Polymer(b2) (A)/(b1) (A)+(b1)/(b2) (A)/(B)														
Comparative Examples	1	a1-1	40	a2-1	47	-	0	7	3	3	p-2	3	-	-	b1-1	b2-1	5	8.50	19.0	5.67	Fair	Very Good	Very Good	Good	36.0	0.85	-	0.85			
	2	a1-1	40	a2-1	47	-	0	7	3	3	p-2	3	-	-	b1-1	b2-1	5	3.75	19.0	3.00	Fair	Very Good	Very Good	Good	36.8	0.85	-	0.85			
	3	a1-1	40	a2-1	47	-	0	7	3	3	p-2	3	-	-	-	-	0	-	-	-	Fair	Very Good	Fair	Fair	34.1	0.85	-	0.85			
	4	a1-1	39	a2-1	46	a3-1	3	6	3	3	p-2	3	-	-	-	-	0	-	-	-	Fair	Poor	Fair	Good	58.8	0.85	15.33	0.80			
	5	a1-1	65	-	0	-	0	22	13	-	0	-	-	-	b1-1	b2-1	53	3.70	0.89	0.59	Good	Good	Fair	Poor	37.6	-	-	-			
	6	a1-1	40	a2-2	47	-	0	7	3	3	p-1	3	-	-	b1-1	b2-1	5	8.50	19.0	5.67	Fair	Good	Good	Very Good	38.1	0.85	-	0.85			
	7	a1-1	40	-	0	a3-1	47	6	3	3	p-2	3	-	-	b1-1	b2-1	5	8.50	19.0	5.67	Poor	Poor	Fair	Very Good	82.1	-	0.00	0.85			
	8	a1-1	15	a2-1	62	a3-1	10	6	3	3	p-2	3	-	-	b1-1	b2-1	5	8.50	19.0	5.67	Good	Poor	Fair	Good	72.4	0.24	6.20	0.21			
	9	a1-1	60	a2-1	17	a3-1	10	6	3	3	p-2	3	-	-	b1-1	b2-1	5	8.50	19.0	5.67	Poor	Poor	Poor	Very Good	79.9	3.53	1.70	2.22			
	10	a1-1	36	a2-1	42	a3-1	10	6	3	3	p-2	3	-	-	b1-1	b2-1	10	0.80	9.00	0.67	Good	Very Good	Good	Poor	66.5	0.86	4.20	0.69			

Comparative Examples

[0070]

From the results shown in Tables 1 and 2, it is found that the biodegradable resin compositions and biodegradable films of the present invention have improved moldability and mechanical characteristics, excellent heat seal characteristics, and a moderate biodegradation rate compared with those of the Comparative Examples.

Industrial Applicability

[0071]

The biodegradable resin composition and biodegradable film of the present invention have a moderate biodegradation rate and hydrolysis rate, and the biodegradable film has strong tear strength, particularly in the machine (stretching) direction, and is preferably used as compost bags, agricultural films, packaging materials, and the like.

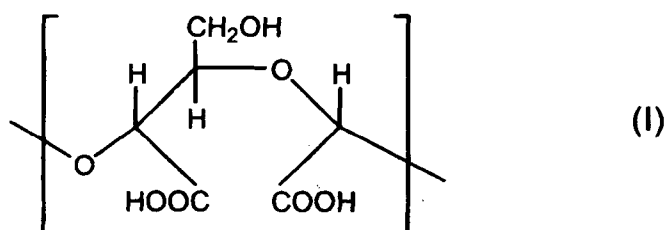
CLAIMS

[Claim 1]

A biodegradable resin composition comprising:
 a composition (A) comprising
 starch (a1),
 a condensation polymer (a2) of an aliphatic diol and an aliphatic dicarboxylic acid, and
 a condensation polymer (a3) of an aliphatic diol, a tri- to hexa-functional aliphatic alcohol, and an aliphatic dicarboxylic acid; and
 a composition (B) being at least one of an amorphous polylactic acid polymer (b1) and an aliphatic aromatic polyester (b2), wherein
 a mass ratio $[(a1)/\{(a2) + (a3)\}]$ is in the range of 0.25 to 2.20, and a mass ratio $[(A)/(B)]$ is in the range of 1 to 35.

[Claim 2]

The biodegradable resin composition according to claim 1, wherein the starch (a1) is oxidized starch having a repeating structure represented by the following general formula (I):



[Claim 3]

The biodegradable resin composition according to claim 1, wherein the starch (a1) is oxidized starch produced using sodium hypochlorite.

[Claim 4]

The biodegradable resin composition according to claim 1, wherein a mass ratio of the condensation polymer (a2) to the condensation polymer (a3), $[(a2)/(a3)]$, is in the range of 0.5 to 12.

[Claim 5]

The biodegradable resin composition according to claim 1, wherein a mass ratio of the aliphatic diol to the tri- to hexa-functional aliphatic alcohol, [the aliphatic diol/the tri- to hexa-functional aliphatic alcohol], in the condensation polymer (a3) is in the range of 4 to 200.

[Claim 6]

The biodegradable resin composition according to claim 1, wherein in the condensation polymer (a2), the aliphatic diol is one or more selected from ethylene glycol and 1,4-butanediol, and the aliphatic dicarboxylic acid is one or more selected from succinic acid and adipic acid.

[Claim 7]

The biodegradable resin composition according to claim 1, wherein in the condensation polymer (a3), the aliphatic diol is one or more selected from ethylene glycol and 1,4-butanediol, the aliphatic dicarboxylic acid is one or more selected from succinic acid and adipic acid, and the tri- to hexa-functional aliphatic alcohol is trimethylolpropane.

[Claim 8]

The biodegradable resin composition according to claim 1, wherein the amorphous polylactic acid polymer (b1) is a polymer of L-lactic acid and D-lactic acid, and a content of the L-lactic acid and a content of the D-lactic acid are each 94 mol % or less.

[Claim 9]

The biodegradable resin composition according to claim 1, wherein the aliphatic aromatic polyester (b2) is one or more selected from a condensation polymer of an aliphatic polyol and an aromatic polycarboxylic acid, and a condensation polymer of an aliphatic polyol, an aliphatic polycarboxylic acid, and an aromatic polycarboxylic acid.

[Claim 10]

The biodegradable resin composition according to claim 1, wherein the composition (A) further comprises a solvent having a boiling point of 180°C or more.

[Claim 11]

The biodegradable resin composition according to claim 1, wherein the composition (A) further comprises a plasticizer.

[Claim 12]

The biodegradable resin composition according to claim 11, wherein the plasticizer is one or more selected from polyglycerin acetate, a derivative thereof, and an adipic acid diester.

[Claim 13]

The biodegradable resin composition according to claim 1, wherein the composition (A) comprises a composition obtained by melting and kneading by an extruder with a vent.

[Claim 14]

A biodegradable film using the biodegradable resin composition according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2016/057883A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L3/00 C08L67/02
ADD.

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)
C08L

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

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

EPO-Internal, BIOSIS, EMBASE, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 781 551 A1 (SHOWA DENKO KK [JP]) 24 September 2014 (2014-09-24) paragraph [0034]; claims 1-11 -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2016/057883

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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