

DESCRIPTION

Title of Invention

STYRENE FOAM SHEET AND MOLDED ARTICLE USING SAME

Technical Field

[0001]

The present invention relates to a foam sheet formed by foaming a styrene-based resin composition containing a styrene-based resin and polylactic acid, and a molded article obtained by molding the same.

Background Art

[0002]

In recent years, even general consumers have recognized that it is preferable to use a plastic product including various polymers having biodegradability, from a viewpoint of the protection of environment and it is preferable to use a plant-derived raw material, from a viewpoint of conservation of oil resources, and therefore, experiments using biodegradable polymers or plant-derived polymers as raw materials in industrial products are widely performed.

[0003]

Particularly, polylactic acid is a polymer derived from plants and having biodegradability, and is recognized as a polymer having excellent practicality among the biodegradable

polymers, from a viewpoint of having all of a comparatively high melting point, toughness, transparency, and chemical resistance.

[0004]

Meanwhile, a styrene-based resin is excellent in molding workability and practical mechanical properties such as rigidity. In addition, the styrene-based resin is a resin which is easily foamed, thereby being capable of reducing the weight of a molded article, and significantly contributing to resource saving. Further, a recycling system thereof is established, and the recycling rate is comparatively higher than those of other materials.

[0005]

From such viewpoints, studies for ensuring fluidity and improving mechanical properties by mixing a styrene-based resin and polylactic acid with each other have been performed (for example, see PTL 1). However, the compatibility between a styrene-based resin and polylactic acid is considerably poor, and particularly, when the percentage of polylactic acid is high, it is difficult to design a product having the physical properties desired in the market and utilizing the properties of each resin, only by simply compounding and melt blending.

[0006]

In addition, polylactic acid has poor foaming properties, and therefore, foaming hardly occurs in general extrusion

foaming.

Citation List

Patent Literature

[0007]

[PTL 1] JP-A-2008-50426

Summary of Invention

Technical Problem

[0008]

In consideration of these circumstances, an object of the invention is to provide a styrene foam sheet which is foamed by using a styrene-based resin composition containing a styrene-based resin and polylactic acid in combination without impairing the usefulness of each of the styrene-based resin and polylactic acid, and a molded article obtained by thermoforming the same.

Solution to Problem

[0009]

As a result of intensive studies for achieving the object, the inventors have found that it is possible to provide a styrene foam sheet having excellent foam molding properties, heat resistance, and oil resistance by using a styrene-based resin and a styrene-acrylic ester copolymer as an impact-resistant styrene-based resin, and using a mixture of these resins and polylactic acid, thereby completing the invention.

[0010]

That is, in the invention, a styrene foam sheet formed by foaming a styrene-based resin composition containing an impact-resistant styrene-based resin (A), a styrene-acrylic ester copolymer (B), and polylactic acid (C), and a molded article formed by thermoforming the same are provided.

Advantageous Effects of Invention

[0011]

The styrene foam sheet of the invention has excellent formability, oil resistance, and the like. In addition, the compounding with a plant-derived resin and weight reduction caused by the foaming can reduce environmental loads, and therefore, the styrene foam sheet is preferable from a viewpoint of the protection of environment, and can be suitably used particularly for a food packaging purpose.

Description of Embodiments

[0012]

As an impact-resistant styrene-based resin (A) used in the invention, any resin may be used as long as it is a polystyrene-based resin including a component such as rubber, for example, a generally available resin as a resin being formed by graft polymerization of a rubber-like polymer onto a continuous phase formed of a styrene homopolymer and being in a particle dispersion can be used as it is. Examples of a rubber component included in the impact-resistant styrene-based

resin (A) include polybutadiene, a styrene-butadiene copolymer, polyisoprene, and a butadiene-isoprene copolymer. Particularly, it is preferable that the rubber component is included as polybutadiene or a styrene-butadiene copolymer.

[0013]

The fluidity of the impact-resistant styrene-based resin (A) used in the invention is preferably in a range of 1 to 10 g/10 minutes. from a viewpoint of foam molding stability (thickness stability and cell forming stability).

[0014]

In addition, the content of the rubber-like polymer included in the impact-resistant styrene-based resin (A) is preferably 1.5% to 15.0% by mass, from a viewpoint of satisfying both impact strength and processing characteristics at the time of stretch molding. As the impact-resistant styrene-based resin (A) having such properties, a commercially available product may be used as it is as described above, but a mixture of a general polystyrene and a resin having a high content of a rubber component prepared by adjusting the content of the rubber component or fluidity within the suitable ranges may be used.

[0015]

The styrene-acrylic ester copolymer (B) used in the invention is a copolymer of a styrene-based monomer and an acrylic ester. As the acrylic ester, acrylic acid alkyl ester

is preferable, and acrylic acid alkyl ester in which the number of carbon atoms of an alkyl group is 1 to 20, is more preferable. These may be used alone or in combination of two or more kinds thereof. Among these, methyl acrylate, ethyl acrylate, or butyl acrylate is preferably used, and butyl acrylate is more preferably used.

[0016]

In addition, the fluidity of the styrene-acrylic ester copolymer (B) used in the invention is preferably in a range of 1 to 10 g/10 min. from a viewpoint of foam molding stability or kneading properties.

[0017]

As the polylactic acid (C) used in the invention, a generally available polylactic acid (C) which is obtained by performing saccharification of starch acquired from corns or potatoes, further acquiring lactic acid by lactic acid bacteria, acquiring lactide by cyclization reaction of the lactic acid, and performing a ring-opening polymerization thereof can be used. In addition, polylactic acid obtained by synthesizing lactide from petroleum and performing a ring-opening polymerization thereof, or polylactic acid obtained by obtaining lactic acid from petroleum and directly performing dehydration synthesis thereof may be used.

[0018]

In addition, as the lactic acid constituting the

polylactic acid (C), a mixture of L-lactic acid and D-lactic acid can be used, but, from a viewpoint of excellent heat resistance of a molded article which the resultant composition is formed into, the lactic acid is preferably formed of any one isomer of L-lactic acid and D-lactic acid, and specifically, lactic acid in which the content of D form (the percentage of D-lactic acid with respect to the total mass of lactic acid used as a raw material) is 3.0% or less is preferable.

[0019]

Further, components other than D-lactic acid and L-lactic acid which are main constituent monomers may be copolymerized with the polylactic acid (C). Examples of the other copolymerizable components include ethylene glycol, propylene glycol, butanediol, oxalic acid, adipic acid, and sebacic acid. The content of such a copolymerizable component normally is preferably 0 to 30 mol% and more preferably 0 to 10 mol% with respect to the entire amount of the monomer components.

[0020]

The molecular weight or molecular weight distribution of the polylactic acid (C) is not particularly limited, as long as molding can be substantially performed, and a weight average molecular weight thereof is preferably from 10,000 to 400,000 and more preferably from 40,000 to 200,000.

[0021]

In addition, an additive for preventing thermal degradation of the polylactic acid (C) can be added. Specifically, a carbodiimide-based or an epoxy-based additive is used.

[0022]

A use ratio between the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B), and the polylactic acid (C) is preferably in a range of 99/1 to 85/15, as a mass ratio represented by $[(A) + (B)] / (C)$. More preferably, the total content of the impact-resistant styrene-based resin (A) and the styrene-acrylic ester copolymer (B) is in a range of 97% to 90% by mass and the content of the polylactic acid (C) is in a range of 3% to 10% by mass. Regarding the total content of (A) and (B), a mass ratio represented by $(A) / (B)$ is preferably in a range of 60/40 to 90/10. When the content of the polylactic acid (C) is equal to or smaller than 15% by mass, excellent dispersibility of the resin composition is obtained, foamability is improved, and it is possible to easily obtain a foam sheet. Meanwhile, when the content of the impact-resistant styrene-based resin (A) and the styrene-acrylic ester copolymer (B) is 85% to 99% by mass, and regarding the total content of (A) and (B), the mass ratio represented by $(A) / (B)$ is in a range of 60/40 to 90/10, with respect to a foam sheet to be obtained, mechanical properties can be maintained, a range of formability can be improved, and

heat resistance can be maintained, and the effects of the polylactic acid (C) such as oil resistance can be easily exhibited.

[0023]

In addition, in the invention, the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B), and the polylactic acid (C) are used, however, other resins or various additives may be used in combination, if necessary, to prepare a styrene-based resin composition.

[0024]

Examples of the various additives include an antistatic agent, an antioxidant, an ultraviolet absorber, a lubricant, an anti-blocking agent, and a heat stabilizer.

[0025]

The thickness of the styrene foam sheet of the invention is not particularly limited, but the thickness is preferably in a range of 0.5 to 6.0 mm and more preferably in a range of 0.75 to 3 mm, from viewpoints of handling ability in obtaining a molded article by a secondary process and strength of the molded article.

[0026]

In a case of molding the foam sheet, an extruded foam sheet can be manufactured by a normal foam molding method of allowing the resin to be impregnated with a foaming agent, supplying the resin to an extruder, performing heating, melting,

kneading, and extruding the kneaded components from a circular die or a T-shaped die while foaming.

[0027]

As the foaming agent, a foaming material for general use can be used. Examples thereof include lower hydrocarbons such as propane, butane, pentane, and hexane, halogen hydrocarbons such as methyl chloride, dichloromethane, trichloromonofluoromethane, and dichlorodifluoromethane, and carbon dioxide. In the case of a handling operation in using a general extruder or a low expansion ratio, it is preferable to apply chemical foaming using a sodium bicarbonate-based foaming agent which generates carbon dioxide by heating.

[0028]

In addition, an inorganic compound can be used as a nucleating agent, in order to control the foam cell amount and the size. Talc is exemplified as a preferable inorganic compound.

[0029]

In addition, a mixing order of the resin is not particularly limited, and a method of dry blending the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B), and the polylactic acid (C), then adding a foaming agent thereto, and supplying the components to a melt kneader, or a method of preparing a masterbatch obtained by melting and kneading the impact-resistant styrene-based resin

(A) and the polylactic acid (C) in advance, then melting and kneading the masterbatch, the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B) , and a foaming agent, and then performing foam forming.

[0030]

In addition, if necessary, a method of melting and kneading other additives at the same time, or a method of preparing a masterbatch obtained by melting and kneading the impact-resistant styrene-based resin (A) and other additives in advance, then melting and kneading the masterbatch, the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B), the polylactic acid (C), and a foaming agent, and then performing foam molding, may be employable.

[0031]

In addition, a temperature in melting and kneading the components is preferably in a range of 180°C to 260°C, and from a viewpoint of preventing degradation of the polylactic acid (C) due to heat, a viewpoint of kneading properties of the polylactic acid (C) and the impact-resistant styrene-based resin (A), and the styrene-acrylic ester copolymer (B), and a viewpoint of generation efficiency of carbon dioxide in a case of using a sodium bicarbonate-based foaming agent, the temperature is preferably 180°C to 230°C.

[0032]

A die temperature of the circular die or the T-shaped

die is preferably in a range of 120°C to 150°C, from a viewpoint of performing stable foam molding.

[0033]

The ratio when manufacturing a foam sheet is not particularly limited, and is preferably 1.2 to 3.0 times, from the viewpoint of the balance between maintenance of the mechanical strength, and weight reduction due to foaming and molding properties.

[0034]

The styrene foam sheet obtained as described above can be subjected to a secondary process by thermoforming to obtain a molded article. As the thermoforming method, a hot plate contact thermoforming method, a vacuum forming method, a vacuum/pressure forming method, or a plug-assist forming method is preferably used.

[0035]

The shape of the molded article may be a shape of various packs or cases, and is not particularly limited. The molded article is preferably used for food packaging and particularly preferably used as a container tray or a container, from viewpoints of formability and oil resistance which are characteristics of the styrene foam sheet and the molded article thereof of the invention.

[0036]

A film or a sheet can be bonded to the front and the back

of the obtained foam sheet or the molded article obtained by secondary forming thereof, in order to impart mechanical strength or drug resistance thereto or improve in such properties. Specifically, a polystyrene-based inflation film may be laminated with heat or an olefin-based film (CPP) may be bonded through an adhesive. In addition, a film or a sheet can be bonded at the same time during the in-line of foaming molding.

Examples

[0037]

Hereinafter, the invention will be further described with reference to examples, but the invention is not limited to the examples. Unless otherwise noted, "parts" and "%" are based on mass.

[0038]

Oil resistance, formability, and heat resistance of the obtained sheet were measured and evaluated by the following method.

[0039]

[Oil Resistance]

The obtained styrene foam sheet was cut into a strip having a size of 100 × 20 mm, the strip was wound around a paper tube having a diameter of 90 mm, edible oil (WHITE F-2: Fuji Seiki Co., Ltd.) was applied thereto, the paper tube was stood still in a thermostatic chamber at 25°C, and the time when cracks

were generated on the strip due to aging was confirmed.

[0040]

[Secondary Forming of Foam Article]

The obtained foam sheet was subjected to vacuum forming at a heater temperature of 300°C by using a cup-shaped die having an opening diameter of 80 mm and a depth of 40 mm (drawing ratio of 0.5), and thus, a molded article was obtained.

[0041]

[Evaluation Method at the Time of Secondary Forming]

In a case where sheet tears or cracks did not occur at the time of the secondary forming, the secondary formability was evaluated as "A", in a case where cracks partially occurred, the secondary formability was evaluated as "B", and in a case where tears occurred, the secondary formability was evaluated as "C".

[0042]

[Evaluation Method of Heat Resistance]

The obtained cup-shaped molded article was put in an oven at 80°C, and heated for 10 minutes, and heat resistance was evaluated in terms of a degree of deformation. In a case where the molded article was not substantially deformed, the heat resistance was evaluated as "A", in a case where molded article was deformed to a medium level, the heat resistance was evaluated as "B", and in a case where molded article was greatly deformed, the heat resistance was evaluated as "C".

[0043]

[Fluidity]

The fluidity of the impact-resistant styrene-based resin was measured at 200°C and a load of 5 kg, and the fluidity of the polylactic acid was measured at 210°C and a load of 2.16 kg.

[0044]

As the impact-resistant styrene-based resin (A), the followings were used.

(A-1): a styrene-based resin having fluidity of 2.0 g/10 min and the content of a rubber component in the resin of 7%

(A-2): a styrene-based resin having fluidity of 4.0 g/10 min and the content of a rubber component in the resin of 10%

(A-3): a styrene-based resin having fluidity of 10.0 g/10 min and the content of a rubber component in the resin of 3%

[0045]

A synthesis method of the resin is as follows.

(A-1): 90 parts of a styrene monomer, 10 parts of toluene, 6 parts of butadiene rubber, 300 ppm (monomer ratio) of t-butyl peroxybenzoate were added, a reaction was allowed in a stirring-type reaction bath, at 130°C for 1.5 hours, and at 140°C to 180°C for 3.5 hours, an unreacted monomer and toluene were removed at 230°C and at a degree of vacuum of 70 to 30 Torr., purification was performed, and thus, the resin was obtained.

[0046]

(A-2) : The resin was obtained by performing the synthesis under the same conditions as in the synthesis of (A-1), except the content of the butadiene rubber was changed to 8 parts.

[0047]

(A-3) : The resin was obtained by performing the synthesis under the same conditions as in the synthesis of (A-1), except the content of the butadiene rubber was changed to 2.5 parts.

[0048]

As the styrene-acrylic acid copolymer (B), the following components were used.

(B-1) : a styrene-acrylic acid copolymer having fluidity of 5.0 g/10 min. and a ratio of styrene/butyl acrylate = 93/7.

[0049]

(B-1) : 95 parts of a styrene monomer, 5 parts of butyl acrylate, 10 parts of toluene, and 200 ppm (monomer ratio) of t-butyl peroxybenzoate were added, a reaction was allowed in a stirring-type reaction bath, at 120°C for 1.5 hours, and at 130°C to 170°C for 3.5 hours, an unreacted monomer and toluene were removed at 230°C and at a degree of vacuum of 70 to 30 Torr., purification was performed, and thus, the resin was obtained.

[0050]

The polylactic acid (C) was used (fluidity of 10 g/10 min. (190°C, 21.2 N), D form: 1.4 mol%, weight average molecular

weight: 180,000).

[0051]

As a foaming agent, an endothermic decomposition type sodium bicarbonate-based foaming agent "CELLBORN SC-K" manufactured by Eiwa Chemical Ind. Co., Ltd. was used.

[0052]

As a foam nucleating agent, all-purpose talc was used.

[0053]

Example 1

The dry blending was performed at a ratio of impact-resistant styrene-based resin (A-1)/styrene-acrylic ester copolymer (B-1)/polylactic acid (C)/sodium bicarbonate-based foaming agent/talc being 65/25/10/1.0/2 parts, melting and kneading were performed at 220°C by means of a single screw extruder, the foaming was caused by a T-shaped die having an end set at 140°C, and thus, a sheet having a thickness of 1.5 mm (expansion ratio: 2.0 times) was obtained.

[0054]

Example 2

A foam sheet having a thickness of 1.5 mm (expansion ratio: 2.0 times) was obtained under the same conditions as in Example 1, except that the impact-resistant styrene-based resin was changed to (A-2).

[0055]

Example 3

A foam sheet having a thickness of 1.5 mm (expansion ratio: 2.0 times) was obtained under the same conditions as in Example 1, except the impact-resistant styrene-based resin was changed to (A-3).

[0056]

Example 4

The dry blending was performed at a ratio of impact-resistant styrene-based resin (A-1)/styrene-acrylic ester (B-1)/polylactic acid (C)/sodium bicarbonate-based foaming agent/talc being 75/20/5/1.0/2 parts, melting and kneading were performed at 220°C by means of a single screw extruder, the foaming was caused by a T-shaped die having an end set at 140°C, and thus, a sheet having a thickness of 1.5 mm (expansion ratio: 2.3 times) was obtained.

[0057]

Comparative Example 1

The dry blending was performed at a ratio of impact-resistant styrene-based resin (A-1)/polylactic acid (C)/sodium bicarbonate-based foaming agent/talc being 90/10/2/2 parts, melting and kneading were performed at 220°C by using a single screw extruder, the foaming was caused by a T-shaped die having an end set at 140°C, and thus, a sheet having a thickness of 1.5 mm (expansion ratio: 1.9 times) was obtained.

[0058]

Comparative Example 2

The dry blending was performed at a ratio of impact-resistant styrene-based resin (A-1)/sodium bicarbonate-based foaming agent being 100/2 parts, melting and kneading were performed at 220°C by means of a single screw extruder, the foaming was caused by a T-shaped die having an end set at 140°C, and thus, a sheet having a thickness of 1.5 mm (expansion ratio: 2.8 times) was obtained.

[0059]

Comparative Example 3

The dry blending was performed at a ratio of impact-resistant styrene-based resin (A-1)/polylactic acid (C) being 95/5 parts, melting and kneading were performed at 220°C by means of a single screw extruder, and a sheet having a thickness of 1.5 mm was obtained by using the T-shaped die.

[0060]

The evaluation results are shown in Tables 1 to 2.

[0061]

[Table 1]

	Example 1	Example 2	Example 3	Example 4
Oil resistance (minutes)	100	100	90	85
Secondary formability	A	A	A	A
Heat resistance	A	A	A	A

[0062]

[Table 2]

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Oil resistance (minutes)	80	20	30
Secondary formability	B	A	B
Heat resistance	A	A	A

CLAIMS

[Claim 1]

A styrene foam sheet formed by foaming a styrene-based resin composition containing an impact-resistant styrene-based resin (A), a styrene-acrylic ester copolymer (B), and polylactic acid (C).

[Claim 2]

The styrene foam sheet according to claim 1,
wherein a use ratio between the impact-resistant styrene-based resin (A), the styrene-acrylic ester copolymer (B), and the polylactic acid (C) is in a range of 99/1 to 85/15, as a mass ratio represented by $[(A) + (B)] / (C)$, and a mass ratio represented by $(A) / (B)$ is in a range of 60/40 to 90/10.

[Claim 3]

The styrene foam sheet according to claim 1 or 2,
wherein the impact-resistant styrene-based resin (A) is obtained by graft polymerization of a rubber-like polymer onto a continuous phase formed of a styrene homopolymer.

[Claim 4]

The styrene foam sheet according to any one of claims 1 to 3,

wherein a ratio of composition of raw materials of the styrene-acrylic ester copolymer (B) is in a range of 95/5 to 85/15, as a mass ratio represented by styrene/acrylic ester.

[Claim 5]

The styrene foam sheet according to any one of claims 1 to 4,

wherein an acrylic ester of the styrene-acrylic ester copolymer (B) is butyl acrylate.

[Claim 6]

The styrene foam sheet according to claim 3,

wherein the content of the rubber-like polymer in the impact-resistant styrene-based resin (A) is in a range of 1.5% to 15% by mass.

[Claim 7]

The styrene foam sheet according to any one of claims 1 to 6,

wherein an expansion ratio in foam forming of the impact-resistant styrene-based resin composition is from 1.2 to 3.0 times.

[Claim 8]

The styrene foam sheet according to claim 7,

wherein chemical foaming is performed in the foam forming.

[Claim 9]

A molded article obtained by molding the styrene foam sheet according to any one of claims 1 to 8 by a thermoforming method.

[Claim 10]

The molded article according to claim 9, which is used

for food packaging.