

DESCRIPTION

Title of Invention: STYRENE-BASED FOAMED SHEET AND MOLDED
PRODUCT USING THE SAME

Technical Field

[0001]

The present invention relates to a foamed sheet produced by foaming a styrene-based resin composition containing a styrene-based resin and polylactic acid, and a molded product produced by molding the foamed sheet.

Background Art

[0002]

It has recently become recognized by general consumers that using plastic products containing various polymers with biodegradability is preferred from the viewpoint of environmental protection and using plant-derived materials is preferred from the viewpoint of saving petroleum resources, and attempts have been widely made to use biodegradable polymers and plant-derived polymers as raw materials of industrial products.

[0003]

In particular, polylactic acid is a polymer derived from plants and having biodegradability, and among biodegradable polymers, polylactic acid is recognized as a practically excellent polymer in view of having a relatively high melting point, toughness, transparency, and chemical

resistance.

[0004]

On the other hand, a styrene-based resin is excellent in moldability and in practical physical properties such as rigidity etc. Also, a styrene-based resin is a resin which can be easily foamed and can produce lightweight molded products and greatly contribute to resource saving. Further, a recycling system is established, and a recycling rate is high as compared with other materials.

[0005]

From this viewpoint, for example, investigation is performed for securing flowability and improving mechanical physical properties by mixing a styrene-based resin and polylactic acid (refer to, for example, Patent Literature 1). However, a styrene-based resin and polylactic acid have very low compatibility therebetween, and in particular, a high ratio of polylactic acid makes it difficult that a product utilizing the physical properties required by the market and the characteristics of each resin is designed by only simple mixing/melt mixing.

[0006]

Also, polylactic acid has poor foaming characteristics and is difficult to foam by general extrusion foaming.

Citation List

Patent Literature

[0007]

PTL 1: Japanese Unexamined Patent Application

Publication No. 2008-50426

Summary of Invention

Technical Problem

[0008]

In consideration of the present situation described above, a problem to be solved by the present invention is to provide a styrene-based foamed sheet produced by foaming a styrene-based resin composition using a styrene-based resin and polylactic acid without impairing the usefulness thereof, and to provide a molded product produced by thermoforming the foamed sheet.

Solution to Problem

[0009]

As a result of repeated earnest investigations for solving the problem, the inventors found that a styrene-based foamed sheet having excellent foam moldability, heat resistance, and oil resistance can be provided by using an impact-resistant styrene-based resin and a highbranched styrene-acrylic acid ester copolymer as a styrene-based resin and mixing with polylactic acid, leading to the achievement of the present invention.

[0010]

That is, the present invention provides a styrene-based

foamed sheet produced by foaming a styrene-based resin composition containing an impact-resistant styrene-based resin (A), a styrene-acrylic acid ester copolymer (B) having a highbranched structure, and polylactic acid (C), and also provides a molded product produced by thermoforming the foamed sheet.

Advantageous Effects of Invention

[0011]

A styrene-based foamed sheet according to the present invention has good moldability, oil resistance, etc. Also, environmental load can be decreased by light-weighting due to mixing and foaming a plant-derived resin, and thus the styrene-based foamed sheet is preferred from the viewpoint of environmental protection and can be particularly preferably used for food packaging application.

Brief Description of Drawings

[0012]

[Fig. 1] Fig. 1 is a chromatogram of molecular weight measurement by GPC-MALLS.

[Fig. 2] Fig. 2 is a log-log graph in which the molecular weight of highbranched styrene-acrylic acid ester copolymer determined by GPC-MALLS is shown on the abscissa, and the inertia radius is shown on the ordinate.

[Fig. 3] Fig. 3 is a schematic drawing of an apparatus for continuous bulk polymerization for a highbranched

styrene-acrylic acid ester copolymer.

Description of Embodiments

[0013]

An impact-resistant styrene-based resin (A) used in the present invention may be a polystyrene-based resin containing rubber or the like as a component. For example, it is possible to directly use a resin which can be generally obtained as a resin produced by graft polymerization of a rubber polymer onto a continuous phase composed of a styrene homopolymer and which contains dispersed particles. Examples of the rubber component contained in the impact-resistant styrene-based resin (A) include polybutadiene, styrene-butadiene copolymer, polyisoprene, butadiene-isoprene copolymer, and the like. In particular, the rubber component is preferably contained as polybutadiene or styrene-butadiene copolymer.

[0014]

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

[0015]

In addition, the content of the rubber polymer contained in the impact-resistant styrene-based resin (A) is

preferably 1.5% to 15.0% by mass from the viewpoint of satisfying both impact strength and processing characteristics during stretch molding. The commercial product described above may be directly used as the impact-resistant styrene-based resin (A) having these characteristics, but a resin containing a rubber component at a high content may be used, in which the rubber component content and flowability are adjusted in respective preferred ranges by mixing general polystyrene.

[0016]

The highbranched styrene-acrylic acid ester copolymer (B) used in the present invention is a copolymer produced by copolymerizing a highbranched macromonomer (b1) having a plurality of branches and a plurality of polymerizable double bonds with a styrene-based monomer (b2) and an acrylic acid ester (b3).

[0017]

Examples of the styrene-based monomer (b1) include the following compounds. Examples of styrene and its derivatives include styrene, alkylstyrene such as methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, triethylstyrene, propylstyrene, butylstyrene, hexylstyrene, heptylstyrene, and octylstyrene, halogenated styrene such as fluorostyrene, chlorostyrene, bromostyrene, dibromostyrene, and iodostyrene, nitrostyrene,

acetylstyrene, methoxystyrene, and the like. These can be used alone or in combination of two or more. Further, the styrene-based monomer (a1) may be used in combination with a compound copolymerizable with the styrene-based monomer (a1), for example, a vinyl monomer such as acrylonitrile, methacrylonitrile, an ester derivative such as methyl methacrylate, butyl acrylate, or the like, maleic anhydride, maleimide, nuclear-substituted maleimide, or the like.

[0018]

The acrylic acid ester (b3) is preferably an acrylic acid alkyl ester in which an alkyl group more preferably has 1 to 20 carbon atoms. These may be used alone or in combination of two or more. Among these, methyl acrylate, ethyl acrylate, or butyl acrylate is preferably used, and butyl acrylate is more preferably used.

[0019]

The highbranched styrene-acrylic acid ester copolymer (B) essentially contains as a highbranched copolymer (B1) which is a copolymer of the highbranched macromonomer (b1) having a plurality of branches and a plurality of polymerizable double bonds with the styrene-based monomer (b2) and the acrylic acid ester (b3), and may contain a linear copolymer of the styrene-based monomer (b2) and the acrylic acid ester (b3), which is produced at the same time as copolymerization, and may further contain a homopolymer

of the styrene-based monomer (b2) and a homopolymer of the acrylic acid ester (b3).

[0020]

The highbranched styrene-acrylic acid ester copolymer (B) used in the present invention preferably has a weight-average molecular weight of 150,000 to 700,000 determined by a GPC-MALLS method and more preferably within a range of 200,000 to 600,000 from the viewpoint of productivity and processability. The highbranched copolymer (B1) preferably has a weight-average molecular weight of 1,000,000 to 10,000,000 determined by GPC-MALLS, and the linear copolymer preferably has a weight-average molecular weight of 100,000 to 450,000 determined by GPC-MALLS.

[0021]

[GPC-MALLS]

When the molecular weight of the highbranched styrene-acrylic acid ester copolymer (B) used in the present invention is measured by GPC-MALLS, for example, a chromatogram shown in Fig. 1 is obtained. In Fig. 1, P1 is a peak on the low-molecular-weight side, and P2 is a peak on the high-molecular-weight side. The peak P1 is supposed to be due to a linear resin and a resin with a low branching degree, and the peak P2 is supposed to be mainly due to a highbranched resin with a high branching degree. The region of the peak P2 is formed by a region (1) surrounded by a

perpendicular line drawn down from the highest point of the peak 2 to a baseline (in Fig. 1, a dotted line drawn substantially parallel to the volume axis), the baseline, and a molecular weight curve on the left side of the highest point, and a region (2) surrounded by a molecular weight curve (in Fig. 1, a virtual molecular weight curve shown by a dotted line on the right side of the perpendicular line) formed by folding back the region (1) to the right side along the perpendicular line as a symmetrical axis, the perpendicular line, and the baseline. The region of the peak P1 is a portion obtained by subtracting the region of the peak P1 including the region (1) and the region (2) from a region surrounded by the molecular weight curve and the baseline.

[0022]

[Mixing ratio between resin in peak P1 region and resin in peak P2 region]

The mass ratio between the resin in the region of the peak P1 to the resin in the region of the peak P2 in the highbranched styrene-acrylic acid ester copolymer (B) used in the present invention is preferably (resin in peak P2 region)/(resin in peak P1 region) = 30/70 to 70/30 and more preferably 40/60 to 60/40 in view of excellent balance between the strength and processability of the resultant sheet. The ratio can be easily controlled by adjusting the

use ratio of the highbranched macromonomer (b1) to the styrene-based monomer (b2) and the acrylic acid ester (b3) and the type and amount of the chain transfer agent used.

[0023]

[Gradient of log-log graph of highbranched styrene-acrylic acid ester copolymer (B)]

Also, in a log-log graph in which the molecular weight of the highbranched styrene-acrylic acid ester copolymer (B) used in the preset invention determined by GPC-MALLS is shown on the abscissa, and the inertia radius is shown on the ordinate, the gradient within a molecular weight region of 250,000 to 10,000,000 is most preferably 0.25 to 0.55 from the viewpoint of exhibiting the excellent balance between strength and moldability. When the gradient is larger than 0.55, the physical properties become closer to those of a linear resin, while conversely when the gradient is smaller than 0.25, flowability may be decreased due to an increase in molecular weight accompanying an increase in branching degree.

[0024]

[Highbranched macromonomer (b1)]

The highbranched macromonomer (b1) used in the present invention, which has a plurality of branches and a plurality of polymerizable double bonds, preferably has a weight-average molecular weight (Mw) within a range of 1,000 to

15,000 and more preferably 3,000 to 8,000 from the viewpoint of easily producing a styrene-based resin composition exhibiting the excellent characteristics described above when formed into a foamed sheet and from the viewpoint of suppressing the occurrence of a gel and securing flowability by controlling the weight-average molecular weight of the highbranched copolymer (B1) to 10,000,000 or less.

[0025]

Preferred examples of the branched structure of the highbranched macromonomer (b1) include, but are not particularly limited to, a branch formed by a quaternary carbon atom to which all of an electron attracting group and the three bonds other than the bond to the electron attracting group are bonded, and a branched structure formed by repeating a structural unit having an ether bond, an ester bond, or an amide bond.

[0026]

In the case of the highbranched macromonomer (b1) having the branched structure formed by the quaternary carbon, the content of the electron attracting group is preferably within a range of 2.5×10^{-4} mmol to 5.0×10^{-1} mmol and more preferably within a range of 5.0×10^{-4} mmol to 5.0×10^{-2} mmol per g of the highbranched macromonomer (b1).

[0027]

It is essential for the highbranched macromonomer (b1)

to have two or more polymerizable double bonds per molecule. The content of the polymerizable double bonds is preferably within a range of 0.1 to 5.5 mmol and more preferably within a range of 0.5 to 3.5 mmol per g of the macromonomer (b1). The content lower than 0.1 mmol tends to caused difficulty in producing the highbranched copolymer (B1) having a high molecular weight, while the content exceeding 5.5 mmol tends to excessively increase the molecular weight of the highbranched copolymer (B1). Also, the polymerizable double bonds are preferably present at the ends of the highbranched macromonomer (b1).

[0028]

The highbranched macromonomer (b1) which can be used in the present invention is for example, a highbranched macromonomer (b1-i) which has a branched structure formed by repeating a structural unit having an ester bond, an ether bond, or an amide bond and has two or more double bonds at the branch ends in one molecule.

[0029]

A highbranched macromonomer (b1-i-1) which has a branched structure formed by repeating a structural unit having an ester bond preferably has, for example, a form in which a polymerizable double bond such as a vinyl group or isopropenyl group is introduced into a highbranched polyester polyol having a quaternary carbon atom as a carbon

atom adjacent to a carbonyl group of an ester bond which forms a molecular chain. A polymerizable double bond can be introduced into a highbranched polyester polyol by esterification reaction or addition reaction.

[0030]

The highbranched polyester polyol may have a substituent previously introduced into some of its hydroxyl groups by an ether bond or another bond. Also, some of the hydroxyl groups may be modified by oxidation reaction or another reaction. Further, some of the hydroxyl groups of the highbranched polyester polyol may be previously esterified.

[0031]

The highbranched macromonomer (b1-i-1) is, for example, one produced by reacting a compound having one or more hydroxyl groups with a monocarboxylic acid having a quaternary carbon atom as a carbon atom adjacent to a carboxyl group and having two or more hydroxyl groups to produce a highbranched polymer and then reacting a hydroxyl group as a terminal group of the polymer with an unsaturated acid such as acrylic acid, methacrylic acid, or the like, an isocyanate group-containing acrylic compound, or the like. A highbranched polymer having a branched structure formed by repeating a structural unit having an ester bond is described in Tamalia, et al., "Angew. Chem. Int. Ed. Engl.

29" p. 138-177 (1990).

[0032]

Examples of the compound having one or more hydroxyl groups include a) aliphatic diol, alicyclic diol, or aromatic diol, b) triol, c) tetraol, d) sugar alcohols such as sorbitol, mannitol, and the like, e) anhydro-enneaheptitol or dipentaerythritol, f) α -alkylglycoside such as α -methylglycoside or the like, g) monofunctional alcohol such as ethanol, hexanol, or the like, h) a hydroxyl group-containing polymer produced by reacting an alkylene oxide having a weight-average molecular weight of at most 8,000 or its derivative with hydroxyl groups of one or more compounds selected from a) to g), and the like.

[0033]

Examples of the a) aliphatic diol, alicyclic diol, or aromatic diol include 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, polytetrahydrofuran, dimethylolpropane, neopentylpropane, 2-propyl-2-ethyl-1,3-propanediol, 1,2-propanediol, 1,3-butanediol, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol; cyclohexanedimethanol, 1,3-dioxane-5,5-dimethanol; 1,4-xylylenedimethanol, 1-phenyl-1,2-ethanediol, and the like. Examples of the b) triol include trimethylolpropane, trimethylolethane, trimethylolbutane,

glycerol, 1,2,5-hexanetriol, 1,3,5-trihydroxybenzene, and the like. Examples of the c) tetraol include pentaerythritol, ditrimethylolpropane, diglycerol, ditrimethylolethane, and the like.

[0034]

Examples of the monocarboxylic acid having a quaternary carbon atom as a carbon atom adjacent to a carboxyl group and having two or more hydroxyl groups include dimethylolpropionic acid, α,α -bis(hydroxymethyl)butyric acid, α,α,α -tris(hydroxymethyl)acetic acid, α,α -bis(hydroxymethyl)valeric acid, α,α -bis(hydroxymethyl)propionic acid, and the like. By using the monocarboxylic acid, ester decomposition reaction can be suppressed, and the highbranched polyester polyol can be formed.

[0035]

In producing the highbranched polyester polyol, a catalyst is preferably used, and examples of the catalyst include organic tin compounds such as dialkyltin oxides, dialkyltin halides, dialkyltin biscarboxylates, stannoxane, and the like, titanates such as tetrabutyl titanate and the like, organic sulfonic acids such as a Lewis acid, paratoluenesulfonic acid, and the like, and the like.

[0036]

A highbranched macromonomer (b1-i-2) which has a

branched structure formed by repeating a structural unit having an ether bond is, for example, one produced by reacting a compound having one or more hydroxyl groups or cyclic ether compounds with a cyclic ether compound having one or more hydroxyl groups to form a highbranched polymer and then reacting a hydroxyl group as a terminal group of the polymer with an unsaturated acid such as acrylic acid, methacrylic acid, or the like, an isocyanate group-containing acrylic compound, or halogenated methylstyrene such as 4-chloromethylstyrene or the like. A method useful for producing the highbranched polymer is a method of reacting a compound having one or more hydroxyl groups with a compound having two or more hydroxyl groups and a halogen atom, $-\text{OSO}_2\text{OCH}_3$, or $-\text{OSO}_2\text{CH}_3$ based on the Williamson ether synthesis method.

[0037]

Any one of the compounds described above can be used as the compound having one or more hydroxyl groups, and examples of the cyclic ether compound having one or more hydroxyl groups include 3-ethyl-3-(hydroxymethyl)oxetane, 2,3-epoxy-1-propanol, 2,3-epoxy-1-butanol, 3,4-epoxy-1-butanol, and the like. Any one of the compounds described above may be used as the compound having one or more hydroxyl groups used in the Williamson ether synthesis method, but an aromatic compound having two or more hydroxyl

groups bonded to an aromatic ring is preferred. Examples of the compound include 1,3,5-trihydroxybenzene, 1,4-xylylenedimethanol, 1-phenyl-1,2-ethanediol, and the like. Examples of the compound containing two or more hydroxyl groups and a halogen atom, $-\text{OSO}_2\text{OCH}_3$, or $-\text{OSO}_2\text{CH}_3$ include 5-(bromomethyl)-1,3-dihydroxybenzene, 2-ethyl-2-(bromomethyl)-1,3-propanediol, 2-methyl-2-(bromomethyl)-1,3-propanediol, 2-(bromomethyl)-2-(hydroxymethyl)-1,3-propanediol, and the like. In producing the highbranched polymer, a catalyst is preferably used, and examples of the catalyst include BF_3 diethyl ether, FSO_3H , ClSO_3H , HClO_4 , and the like.

[0038]

A highbranched macromonomer (b1-i-3) which has a branched structure formed by repeating a structural unit having an amide bond is, for example, one having a repeating structure having an amide bond through a nitrogen atom in its molecule, and a typical example thereof is Generation 2.0 (PAMAM dendrimer) manufactured by Dentoritech Co., Ltd.

[0039]

[Method for polymerizing highbranched macromonomer (b1), styrene-based monomer (b2), and acrylic acid ester (b3)]

A resin mixture containing a highbranched resin and a linear resin and low-branched resin, which are simultaneously produced depending on the polymerization

conditions, can be produced by copolymerizing the highbranched macromonomer (b1), the styrene-based monomer (b2), the acrylic acid ester (b3), and another monomer combined according to demand. The highbranched macromonomer (b1) is used preferably at a ratio of 50 ppm to 1% and more preferably 100 ppm to 3000 ppm (mass basis) to the total amount of the styrene-based monomer (b2) and the acrylic acid ester (b3) because the highbranched resin can be easily produced, and thus the highbranched styrene-acrylic acid ester copolymer (B) used in the present invention can be easily produced.

[0040]

The use ratio of the styrene-based monomer (b2) to the acrylic acid ester (b3) is preferably within a range of 95/5 to 85/15 in terms of mass ratio of styrene-based monomer (b2)/acrylic acid ester (b3) because a sheet produced by using the resultant composition has more excellent heat resistance and secondary molding has good moldability.

[0041]

Various methods generally used for polymerizing a styrene-based monomer can be used for polymerization reaction. The polymerization method is not particularly limited, but is preferably bulk polymerization, suspension polymerization, or solution polymerization. Among these, continuous bulk polymerization is preferred in view of

production efficiency, and an excellent resin can be produced by, for example, continuous bulk polymerization using one or more stirring-type reactors and a tubular reactor in which a plurality of mixing elements are fixed without a movable portion. Thermal polymerization can be performed without using a polymerization initiator, but any one of various radical polymerization initiators is preferably used. In addition, a polymerization auxiliary which is generally used for producing polystyrene, such as a suspending agent, an emulsifier, or the like necessary for polymerization, can be used.

[0042]

An organic solvent may be added to the reaction system in order to decrease the viscosity of the reaction product of polymerization reaction, and examples of the organic solvent include toluene, ethylbenzene, xylene, acetonitrile, benzene, chlorobenzene, dichlorobenzene, anisole, cyanobenzene, dimethylformamide, N,N-dimethylacetamide, methyl ethyl ketone, and the like. In particular, when the amount of the highbranched macromonomer added is desired to be increased, the organic solvent is preferably used from the viewpoint of suppressing gelation. Therefore, the amount of the highbranched macromonomer (b1) added described above can be remarkably increased, thereby permitting the introduction of many branched structures and preventing the

occurrence of gelation.

[0043]

Examples of the radical polymerization initiator include, but are not limited to, peroxyketals such as 1,1-bis(tert-butylperoxy)cyclohexane, 2,2-bis(tert-peroxy)butane, 2,2-bis(4,4-di-butylperoxycyclohexyl)propane, and the like; hydroperoxides such as cumene hydroperoxide, tert-butyl hydroperoxide, and the like; dialkyl peroxides such as di-tert-butyl peroxide, dicumyl peroxide, di-tert-hexyl peroxide, and the like; diacyl peroxides such as benzoyl peroxide, dicinnamoyl peroxide, and the like; peroxyesters such as tert-butyl peroxybenzoate, di-tert-butyl peroxyisophthalate, tert-butyl peroxyisopropyl monocarbonate, and the like; N,N'-azobisisobutyronitrile, N,N'-azobis(cyclohexane-1-carbonitrile), N,N'-azobis(2-methylbutyronitrile), N,N'-azobis(2,4-dimethylvaleronitrile), N,N'-azobis[2-(hydroxymethyl)propionitrile], and the like. These can be used alone or in combination of two or more.

[0044]

Further, a chain transfer agent may be added for preventing an excessive increase in molecular weight of the resultant resin composition. Either a monofunctional chain transfer agent having one chain transfer group or a polyfunctional chain transfer agent having a plurality of chain transfer groups may be used as the chain transfer

agent. Examples of the monofunctional chain transfer agent include alkyl mercaptans, thioglycolic acid esters, and the like. Examples of the polyfunctional chain transfer agent include that produced by esterifying hydroxyl groups in polyhydric alcohol such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, or the like with thioglycolic acid or 3-mercaptopropionic acid, and the like.

[0045]

Further, a long-chain alcohol, a polyoxyethylene alkyl ether, a polyoxyethylene lauryl ether, a polyoxyoleyl ether, a polyoxyethylene alkenyl ether, or the like can be used for suppressing the occurrence of gelation of the resultant resin composition.

[0046]

<Polymerization step>

In the polymerization step, the highbranched macromonomer (b1), the styrene-based monomer (b2), and the acrylic acid ester (b3) are used as monomer components, and copolymerization of these components can produce a styrene-based resin composition containing the highbranched copolymer (B1) which is a copolymer of these three components. Fig. 3 shows an example of a reactor of a polymerization apparatus for producing the resin composition in the present invention. That is, a reaction solution is

sent to a stirring-type reactor (I) by a pump (1), next sent to a circulation polymerization line (II) by a pump (2), circulated in the circulation polymerization line by a pump (3), and then after circulation, sent to a non-circulation polymerization line (III). The circulation polymerization line (II) includes three reactors (4) to (6), and the non-circulation polymerization line (III) includes three reactors (7) to (9).

[0047]

Also, if required, a monomer and a solvent can be further added to between the stirring-type reactor (I) and the circulation polymerization line (II) and between the circulation polymerization line (II) and the non-circulation polymerization line (III).

[0048]

<Devolatilization step>

After the polymerization step, a devolatilization tank 1 and a devolatilization tank 2 are connected for volatilizing the unreacted monomers and the solvent. The devolatilization tanks 1 and 2 are preferably adjusted to be under reduced-pressure conditions of 4.0 kPa and 1.3 kPa, respectively, and pellets are formed after passage through the devolatilization tank 1 and the devolatilization tank 2. Consequently, the highbranched styrene-acrylic acid ester copolymer (B) used in the present invention can be produced.

[0049]

The flowability of the highbranched styrene-acrylic acid ester copolymer (B) used in the present invention is preferably within a range of 1 to 10 g/10 min. from the viewpoint of foam molding stability and kneadability.

[0050]

A usable example of polylactic acid (C) used in the present invention is polylactic acid (C) which is generally available and produced by saccharifying starch obtained from corns, potatoes, etc., forming lactic acid by using lactobacillus, next forming a lactide by cyclization reaction of lactic acid, and then carrying out ring-opening polymerization of the lactide. Also, the polylactic acid (C) used may be polylactic acid produced by synthesizing lactide from petroleum and then carrying out ring-opening polymerization of the lactide or polylactic acid produced by producing lactic acid from petroleum and then performing direct dehydration condensation of lactic acid.

[0051]

The lactic acid constituting the polylactic acid (C) can also be used as a mixture of L-lactic acid and D-lactic acid, but is preferably composed of either of the L-lactic acid and D-lactic acid isomers in view of excellent heat resistance of a molded product produced by molding the composition. Specifically, the content of the D-isomer

(content of D-lactic acid relative to the total mass of the lactic acid used as a raw material) is preferably 3.0% or less.

[0052]

Further, the polylactic acid (C) may contain another component copolymerized with D-lactic acid and L-lactic acid as the main constituent monomers. Examples of the other copolymerization component include ethylene glycol, propylene glycol, butanediol, oxalic acid, adipic acid, sebacic acid, and the like. The content of the copolymerization component generally preferably 0 to 30 mol% and more preferably 0 to 10 mol% of all monomer components.

[0053]

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

[0054]

Also, an additive for suppressing thermal deterioration of the polylactic acid (C) can be added. Specifically, a carbodiimide-based or epoxy-based additive can be added.

[0055]

The use ratio between the impact-resistant styrene-

based resin (A), the highbranched styrene-acrylic acid ester copolymer (B), and the polylactic acid (C) is preferably within a range of 99/1 to 85/15 in terms of mass ratio represented by $[(A) + (B)]/(C)$. More preferably, the total of the impact-resistant styrene-based resin (A) and the highbranched styrene-acrylic acid ester copolymer (B) is within a range of 97% to 90% by mass, and the polylactic acid (C) is within a range of 3% to 10% by mass. The mass ratio of (A)/(B) in the total of (A) and (B) is preferably within a range of 60/40 to 90/10. The amount of the polylactic acid (C) of 15% by mass or less causes good dispersibility of the resin composition and improves formability, thereby easily producing a foamed sheet. On the other hand, when the total of the impact-resistant styrene-based resin (A) and the highbranched styrene-acrylic acid ester copolymer (B) is within a range of 85% to 99% by mass, and the mass ratio of (A)/(B) in the total of (A) and (B) is within a range of 60/40 to 90/10, the resultant foamed sheet can maintain mechanical physical properties, exhibit an improved moldability range, maintain heat resistance, and exhibit the oil resistance effect of the polylactic acid (C), etc.

[0056]

In addition, the present invention uses the impact-resistant styrene-based resin (A), the highbranched styrene-

acrylic acid ester copolymer (B), and the polylactic acid (C), and if required, the styrene-based resin composition may be prepared by combining another resin and various additives.

[0057]

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

[0058]

The thickness of the styrene-based foamed sheet of the present invention is not particularly limited but is preferably within a range of 0.5 to 6.0 mm and more preferably within a range of 0.75 to 3 mm from the viewpoint of easy handleability in producing a molded product by secondary molding and strength of the molded product.

[0059]

In molding the foamed sheet, an extrusion-foamed sheet can be produced by a usual foam molding method in which the resin is impregnated with a foaming agent, supplied to an extruder, kneaded by heat-melting, and extruded and foamed from a circular die, a T-die, or the like.

[0060]

A general-purpose foaming material can be used as the foaming agent. Examples thereof include lower hydrocarbons such as propane, butane, pentane, hexane, and the like,

halogenated hydrocarbons such as methyl chloride, dichloromethane, trichloromonofluoromethane, dichlorodifluoromethane, and the like, carbon dioxide, and the like. In the case of a handling operation and a low foaming magnification with a usual extruder, chemical foaming with a sodium bicarbonate-based foaming agent which generates carbon dioxide by heating is preferred.

[0061]

Further, an inorganic compound can be used as a nucleation agent for controlling the amount and size of foamed cells. A preferred example of the inorganic compound is talc.

[0062]

Also, the order of mixing of resins is not particularly limited, and examples of a mixing method include a method of dry-blending the impact-resistant styrene-based resin (A), the highbranched styrene-acrylic acid ester copolymer (B) and the polylactic acid (C), adding a foaming agent, and supplying the resultant mixture to a melt kneading machine; a method of melt-kneading the impact-resistant styrene-based resin (A) and the polylactic acid (C) to prepare a master batch, melt-kneading the master batch, the impact-resistant styrene-based resin (A), the highbranched styrene-acrylic acid ester copolymer (B), and a foaming agent, and then foam-molding the resultant mixture; and the like.

[0063]

If required, the method used may be a method of simultaneously melt-kneading other additives, or a method of melt-kneading the impact-resistant styrene-based resin (A) and other additives to prepare a master batch, melt-kneading the master batch, the impact-resistant styrene-based resin (A), the highbranched styrene-acrylic acid ester copolymer (B), the polylactic acid (C), and a foaming agent, and then foam-molding the resultant mixture.

[0064]

Further, the temperature for melt-kneading the components is preferably within a range of 180°C to 260°C, and from the viewpoint of preventing thermal deterioration of the polylactic acid (C), kneadability of the polylactic acid (C), the impact-resistant styrene-based resin (A), and the highbranched styrene-acrylic acid ester copolymer (B), and the generation efficiency of carbon dioxide in the use of the sodium bicarbonate-based foaming agent, the temperature is preferably 180°C to 230°C.

[0065]

The temperature of a die such as a circular die, T-die, or the like is preferably within a range of 120°C to 150°C in view of stable foam molding.

[0066]

In producing the foamed sheet, the magnification is not

particularly limited but is preferably 1.2 to 3.0 times from the viewpoint of maintaining mechanical strength and balance between lightweighting by foaming and moldability.

[0067]

The styrene-based foamed sheet produced as described above can be secondarily processed by thermoforming to produce a molded product. Examples of a thermoforming method which can be preferably used include a hot-plate contact heating forming method, a vacuum forming method, a vacuum pressure forming method, a plug assist forming method, and the like.

[0068]

The shape of the molded product is a pack, a case, or the like and is not particularly limited, and the molded product is preferably used for food packaging and particularly preferably used as a container tray or a container from the viewpoint of moldability and oil resistance which are characteristics of the styrene-based foamed sheet of the present invention and the molded product thereof.

[0069]

In order to improve mechanical strength and chemical resistance, a film or sheet can be laminated on the front/back side of the resultant foamed sheet or the molded product produced by secondary molding the foamed sheet.

Specifically, a polystyrene-based inflation film can be heat-laminated, and an olefin-based film (CPP) can be laminated by using an adhesive. Also, a film or sheet can be laminated simultaneously during inline foam molding.

EXAMPLES

[0070]

The present invention is further described by giving examples below, but the present invention is not limited to these examples. In addition, both "parts" and "%" are on a mass basis unless otherwise specified.

[0071]

The flowability and molecular weight of each of the raw materials used, and the oil resistance, moldability, and heat resistance of the resultant sheet were measured and evaluated by methods described above.

[0072]

[Flowability]

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

[0073]

[GPC-MALLS measurement]

GPC-MALS measurement of the highbranched styrene-acrylic acid ester copolymer was performed by using Shodex

HPLC, detector Wyatt Technology DAWN EOS and Shodex RI-101, column Shodex KF-806L $\times$ 2, and solvent THF under the conditions of a flow rate of 1.0 ml/min. Analysis of GPC-MALLS measurement was performed by using analysis software ASTRA manufactured by Wyatt Corporation, and the weight-average molecular weight of the highbranched styrene-acrylic acid ester copolymer was determined. In addition, in a log-log graph in which the molecular weight of the highbranched styrene-acrylic acid ester copolymer determined by GPC-MALLS is shown on the abscissa, and the inertia radius is shown on the ordinate, the gradient within a molecular weight region of 250,000 to 10,000,000 (gradient of an approximate straight line automatically calculated by the software based on the measurement values of only a straight line portion obtained within the molecular weight region) was determined.

[0074]

[Oil resistance]

The resultant styrene-based foamed sheet was cut in a strip of 100 $\times$ 20 mm which was then wound on a paper tube having a diameter of 90 mm, and cooking oil (White F-2: manufactured by Fujiseiki Inc.) was applied to the strip. Then, the paper tube was allowed to stand in a constant-temperature room at 25°C to confirm the time when a crack occurred in the strip by changes over time.

[0075]

[Secondary molding of foam]

A molded product was produced by vacuum-molding the foamed sheet using a cup-shaped mold having an opening diameter of 80 mm and a depth of 40 mm (drawing ratio 0.5) at a heater temperature of 300°C.

[0076]

[Method for evaluating secondary molding]

When neither breakage nor cracking occurred in the sheet during secondary molding, secondary moldability was evaluated as "A", when partial cracking occurred, secondary moldability was evaluated as "B", and when breakage occurred, secondary moldability was evaluated as "C".

[0077]

[Method for evaluating heat resistance]

The resultant cup-shaped molded product was placed in an oven of 80°C and heated for 10 minutes, and then heat resistance was evaluated by a degree of deformation. When substantially no deformation occurred, heat resistance was evaluated as "A", when a medium degree of deformation occurred, heat resistance was evaluated as "B", and when large deformation occurred, heat resistance was evaluated as "C".

[0078]

The impact-resistant styrene-based resins (A) used include the following.

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

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

(A-3): Styrene-based resin having a flowability of 10.0 g/10 min, and a rubber component content in the resin of 3%
[0079]

The method for synthesizing each of the resins was as follows.

(A-1): The resin was produced by adding 90 parts of styrene monomer, 10 parts of toluene, 6 parts of butadiene rubber, and 300 ppm (monomer ratio) of tert-butyl peroxybenzoate, reacting the components in a stirring-type reaction tank at 130°C for 1.5 hours and at 140°C to 180°C for 3.5 hours, removing the unreacted monomers and toluene at 230°C and a vacuum degree of 70 to 30 Torr, and then purifying the residue.

[0080]

[A-2]: The resin was synthesized under the same conditions as those for (A-1) except using 8 parts of butadiene rubber.

[0081]

[A-3]: The resin was synthesized under the same conditions as those for (A-1) except using 2.5 parts of butadiene rubber.

[0082]

(REFERENCE EXAMPLE 1) Synthesis of highbranched macromonomer (Mm-1)

<Synthesis of highbranched polyether polyol 1>

In a 2-liter flask provided with a stirrer, a thermometer, a dropping funnel, and a condenser, 50.5 g of ethoxylated pentaerythritol (5 mol-ethylene oxide-added pentaerythritol) and 1 g of a BF₃ diethyl ether solution (50%) were added at room temperature and heated to 110°C. Then, 450 g of 3-ethyl-3-(hydroxymethyl)oxetane was slowly added over 25 minutes while heat generation by the reaction was controlled. When heat generation was stopped, the reaction mixture was further stirred at 120°C for 3 hours and then cooled to room temperature. The resultant highbranched polyether polyol had a weight-average molecular weight of 3,000 and a hydroxyl value of 530.

[0083]

<Synthesis of highbranched polyether 1 having methacryloyl group and acetyl group>

In a reactor provided with a stirrer, a thermometer, a Dean-Stark decanter with a condenser, and a gas inlet tube, 50 g of the highbranched polyether polyol produced in <Synthesis of highbranched polyether polyol 1> described above, 13.8 g of methacrylic acid, 150 g of toluene, 0.06 g of hydroquinone, and 1 g of paratoluenesulfonic acid were

added, and the mixed solution was stirred and heated at normal pressured while 7% oxygen-containing nitrogen (v/v) was blown into the mixed solution at a rate of 3 milliliter/min. The heating amount was adjusted so that the amount of distillate in the decanter was 30 g per hour, and heating was continued until the amount of dehydration reached 2.9 g. After the completion of reaction, the reaction solution was cooled once, and 36 g of acetic anhydride and 5.7 g sulfamic acid were added, followed by stirring at 60°C or 10 hours. Then, in order to remove the remaining acetic and hydroquinone, the reaction solution was washed four times with 50 g of a 5% aqueous sodium hydroxide solution, one time with 50 g of a 1% aqueous sulfuric acid solution, and two times with 50 g of water. Then, 0.02 g of methoquinone was added to the resultant organic layer, and the solvent was distilled off under reduced pressure while 7% oxygen-containing nitrogen (v/v) was introduced, thereby producing 60 g of branched polyether having an isopropenyl group and an acetyl group. The weight-average molecular weight of the branched polyether was 3,900, and the rates of isopropenyl group and acetyl group introduced into the branched polyether polyol were 30 mol% and 62 mol%, respectively.

[0084]

(REFERENCE EXAMPLE 2) Synthesis of highbranched macromonomer

(Mm-2)

<Synthesis of highbranched polyether polyol 2>

In a 1000-mL tree-neck flask connected to nitrogen, an air reflux condenser, a magnet-type stirrer, and a thermometer, 1.24 g (8.7 mmol) of boron trifluoride-diethyl ether complex was diluted with 273 g of dried methyl-tert-butyl ether from which peroxide had been removed. In another vessel, 140 g (1.21 mol) of 3-hydroxymethyl-3-ethyloxetane and 70.0 g (1.21 mol) of propylene oxide were mixed, and the resultant mixture was added dropwise to the three-neck flask over 5.5 hours by using a metering pump. In this case, cooling was performed as needed by an ice bath so that the temperature in the system was kept at 20°C. After the completion of addition, 63.0 g (1.08 mol) of propylene oxide was further added dropwise over 3 hours while the temperature in the system kept at 20°C in the same manner, followed by further stirring for 4 hours. Then, 0.620 g (4.4 mmol) of a boron trifluoride-diethyl ether complex was added, and the mixture was further stirred at 20°C for 6 hours. The reaction mixture was adsorbed and removed by adding hydrotalcite in an amount of 10 times the weight of boron trifluoride-diethyl ether complex used in the reaction and performing reflux for 1 hour. After the hydrotalcite was filtered off, methyl-tert-butyl ether was removed to produce 267 g of transparent highbranched

polyether polyol with high viscosity. The highbranched polyether polyol had $M_n = 2,876$ g/mol, $M_w = 7,171$ g/mol, and hydroxyl value = 253 mg·KOH/g, and proton NMR showed 3-hydroxymethyl-3-ethyloxetane : propylene oxide = 1:1.9 on a molar basis.

[0085]

<Synthesis of highbranched polyether 2 having acryloyl group>

In a 500-ml four-neck flask provided with a Dean-Stark tube, a nitrogen/air inlet tube, a stirrer, and a thermometer, 155 g of the highbranched polyether polyol produced in <Synthesis of highbranched polyether polyol 2> described above, 51 g of acrylic acid, 200 g of cyclohexane, 0.21 g of hydroquinone monomethyl ether, and 4 g (12.3 mmol) of dodecylbenzenesulfonic acid serving a catalyst were charged and heated to 82°C in a stream of mixed gas of nitrogen and air at 2:1. Reflux of cyclohexane was started, and water was started to slowly flow out. Then, the temperature was increased to 85°C and reaction was performed for 18 hours, whereby the dehydration amount reached 60% of the theoretical amount, and thus cooling was started. After cooling near to 30°C, the reaction mixture was washed by adding a 5% aqueous sodium hydroxide solution and 15% aqueous NaCl solution. The resultant polymerizable unsaturated group-containing highbranched polyether had a

hydroxyl value of 70 mg·KOH/g and an acrylic group introduction rate of 60% of all hydroxyl groups.

[0086]

(REFERENCE EXAMPLE 3) Synthesis of highbranched macromonomer (Mm-3)

<Synthesis of highbranched polyether 1 having styryl group and acetyl group>

In a reactor provided with a stirrer, a condenser with a drying tube, a dropping funnel, and a thermometer, 50 g of the highbranched polyether polyol produced in <Synthesis of highbranched polyether polyol 1> described above, 100 g of tetrahydrofuran, and 4.3 g of sodium hydride were added and stirred at room temperature. Then, 26.7 g of 4-chlormethylstyrene was added dropwise over 1 hour, and the resultant reaction mixture was further stirred at 50°C for 4 hours. After the completion of reaction, the reaction mixture was cooled once, and 34 g of acetic anhydride and 5.4 g of sulfamic acid were added and stirred at 60°C for 10 hours. Then, tetrahydrofuran was distilled off under reduced pressure, and the resultant mixture was dissolved in 150 g of toluene. In order to remove the remaining acetic acid, the resultant solution was washed four times with 50 g of a 5% aqueous sodium hydroxide solution, one time with 50 g of a 1% aqueous sulfuric acid solution, and two times with 50 g of water. Then, the solvent was distilled off from the

resultant organic layer under reduced pressure, thereby producing 70 g of highbranched polyether having a styryl group and an acetyl group. The resultant highbranched polyether had a mass-average molecular weight of 4,800, and the rates of styryl group and acetyl group introduced into the highbranched polyether polyol were 38 mol% and 57 mol%, respectively.

[0087]

(REFERENCE EXAMPLE 4) Synthesis of highbranched macromonomer (Mm-4)

<Synthesis of highbranched macromonomer having methacryloyl group and acetyl group>

A stirrer, a pressure gauge, a condenser, and a receiving pan were attached to a four-neck flask, and 308.9 g of ethoxylated pentaerythritol and 0.46 g of sulfuric acid were added to the flask. Then, the resultant mixture was heated to 140°C, and 460.5 g of 2,2-di(hydroxymethyl)propionic acid was added over 10 minutes. After 2,2-di(hydroxymethyl)propionic acid was completely dissolved to produce a transparent solution, the pressure was decreased to 30 to 40 mmHg, and reaction was performed under stirring for 4 hours until the acid value was 7.0 mgKOH/g. Then, 921 g of 2,2-di(hydroxymethyl)propionic acid and 0.92 g of sulfuric acid were added to the reaction solution over 15 minutes, and after a transparent solution

was produced, the pressure was decreased to 30 to 40 mmHg, and reaction was performed under stirring for 3 hours, producing polyester polyol. In a reactor provided with a 7% oxygen inlet tube, a thermometer, a Dean-Stark decanter with a condenser, and a stirrer, 10 g of the polyester polyol produced as described above, 1.25 g of dibutyltin oxide, 100 g of methyl methacrylate having an isopropenyl group, and 0.05 g of hydroquinone were added and heated under stirring while 7% oxygen was brown into the mixed solution at a rate of 3 ml/min. The amount of heating was adjusted so that the amount of distillate in the decanter was 15 to 20 g per hour, and the amount of distillate in the decanter was taken out very hour, and reaction was performed for 4 hours while adding methyl methacrylate in an amount corresponding to the distillate. After the completion of reaction, methyl methacrylate was distilled off under reduced pressure, and 10 g of acetic anhydride and 2 g of sulfamic acid were added for capping the remaining hydroxyl groups, followed by stirring at room temperature for 10 hours. After sulfamic acid was removed by filtration and acetic anhydride and acetic acid were distilled off under reduced pressure, the residue was dissolved in 70 g of ethyl acetate, and in order to remove hydroquinone, the resultant solution was washed four times with 20 g of a 5% aqueous sodium hydroxide solution, two times with 20 g of a 7% aqueous sulfuric acid

solution, and two times with 20 g of water. Then, 0.0045 g of methoquinone was added to the resultant organic layer, and the solvent was distilled off under reduced pressure while 7% oxygen was introduced, thereby producing 11 g of highbranched macromonomer (Mm-3) having an isopropenyl group and an acetyl group. The resultant highbranched macromonomer (Mm-3) had a weight-average molecular weight of 3,000, a number-average molecular weight of 2,100, and a double bond introduction amount of 2.00 mmol/g, and the rates of isopropenyl group and acetyl group introduced into the highbranched macromonomer were 55 mol% and 36 mol%, respectively.

[0088]

(REFERENCE EXAMPLE 5) Synthesis of highbranched macromonomer (Mm-5)

<Synthesis of PAMAM dendrimer having styryl group>

In a reactor provided with a stirrer, a condenser with a drying tube, a dropping funnel, and a thermometer, 50 g of a methanol solution (20%) of PAMAM dendrimer (Generation 2.0: manufactured by Dentritech Co., Ltd.) was added, and methanol was distilled off under stirring under reduced pressure. Then, 50 g tetrahydrofuran and 3.0 g of pulverized potassium hydroxide were added, followed by stirring at room temperature. Then, 7.0 g of 4-chlormethylstyrene was added dropwise to the resultant

mixture over 10 minutes, and the resultant reaction mixture was further stirred at 50°C for 3 hours. After the completion of reaction, the reaction mixture was cooled, and the solid was filtered off. Then, tetrahydrofuran was distilled off under reduced pressure to produce 13 g of PAMAM dendrimer having a styryl group. The styryl group content in the resultant dendrimer was 2.7 mmol/g.

[0089]

(REFERENCE EXAMPLE 6) Synthesis of highbranched macromonomer (Mm-6)

<Synthesis of polyether polyol 2 having styryl group and acetyl group>

In a light-shielding reactor capable of being sealed with nitrogen and provided with a stirrer, a condenser, a light-shielding dropping funnel, and a thermometer, 0.5 g of anhydrous 1,3,5-trihydroxybenzene, 29 g of potassium carbonate, 2.7 g of 18-crown-6, and 180 g of acetone were added under a nitrogen stream, and a solution containing 21.7 g of 5-(bromomethyl)-1,3-dihydroxybenzene and 180 g of acetone was added dropwise under stirring over 2 hours. Then, the resultant mixture was heated under stirring and reflux until 5-(bromomethyl)-1,3-dihydroxybenzene disappeared. Then, 9.0 g of 4-chloromethylstyrene was added, and the resultant mixture was heated under stirring and reflux until 4-chloromethylstyrene disappeared. Then, 4 g

of acetic anhydride and 0.6 g sulfamic acid were added to the reaction mixture and stirred overnight at room temperature. After cooling, the solid in the reaction mixture was filtered off, and the solvent was distilled off under reduced pressure. The resultant mixture was dissolved in dichloromethane, and the resultant solution was washed three times with water. Then, the dichloromethane solution was dropped into hexane to precipitate highbranched polyether. The highbranched polyether was filtered off and dried to produce 12 g of highbranched polyether polyol having a styryl group and an acetyl group. The mass-average molecular weight was 3,200, and the content of styryl group was 3.5 mmol/g.

[0090]

(REFERENCE EXAMPLE 7) Synthesis of highbranched macromonomer (Mm-7)

<Synthesis of highbranched polyester polyol having methacryloyl group and acetyl group>

In a reactor provided with a 7% oxygen inlet tube, a thermometer, a Dean-Stark decanter with a condenser, and a stirrer, 10 g of "Boltorn H20", 1.25 g of dibutyltin oxide, 100 g of methyl methacrylate having an isopropenyl group as a functional group (B), and 0.05 g of hydroquinone were added and heated under stirring while 7% oxygen (v/v) was blown into the mixed solution at a rate of 3 ml/min. The

heating amount was adjusted so that the amount of distillate in the decanter was 15 to 20 g per hour, and the distillate in the decanter was taken out every hour. Reaction was performed for 6 hours while adding methyl methacrylate in an amount corresponding the distillate taken out.

[0091]

After the completion of reaction, methyl methacrylate was distilled off under reduced pressure, and 10 g of acetic anhydride and 2 g of sulfamic acid were added for capping the remaining hydroxyl groups, followed by stirring for 10 hours at room temperature. Then, sulfamic acid was removed by filtration, and acetic anhydride and acetic acid were distilled off under reduced pressure. Then, the residue was dissolved in 70 g of ethyl acetate, and in order to remove hydroquinone, the resultant solution was washed four times with 20 g of a 5% aqueous sodium hydroxide solution, two times with 20 g of a 7% aqueous sulfuric acid solution, and two times with 20 g of water. Then, 0.0045 g of methoquinone was added to the resultant organic layer, and the solvent was distilled off under reduced pressure while 7% oxygen was introduced, thereby producing 12 g of highbranched polyester having an isopropenyl group and an acetyl group. The highbranched polyester had a mass-average molecular weight of 2,860 and a number-average molecular weight of 3,770, and the rates of isopropenyl group and

acetyl group introduced into the branched polyester polyol (A) were 55 mol% and 40 mol%, respectively.

[0092]

(REFERENCE EXAMPLE 8) Synthesis of highbranched macromonomer (Mm-8)

<Synthesis of solvent-soluble polyfunctional vinyl compound copolymer>

In a 3.0-L reactor, 3.1 moles (399.4 g) of divinylbenzene, 0.7 moles (95.1 g) of ethylvinyl benzene, 0.3 moles (31.6 g) of styrene, 2.3 moles (463.5 g) of 2-phenoxyethyl methacrylate, and 974.3 g of toluene were added, and 42.6 g of boron trifluoride-diethyl ether complex was added at 50°C and reacted for 6.5 hours. After polymerization reaction was terminated by an aqueous sodium hydrogen carbonate solution, the reaction mixture was washed three times with pure water and then poured into a large amount of methanol at room temperature, thereby precipitating a polymer. The resultant polymer was washed with methanol, filtered off, dried, and weighed to produce 372.5 g of polyfunctional vinyl-aromatic copolymer. The weight-average molecular weight M_w of the polyfunctional vinyl copolymer was 8,000, the molar ratio of a structural unit containing a vinyl group derived from a divinyl compound was 0.44, the molar ratio of a terminal double bond derived from 2-phenoxyethyl methacrylate was 0.03, and the

total molar ratio of the both was 0.47.

[0093]

Copolymers prepared as the highbranched styrene-acrylic acid ester copolymer (B) were the following.

[0094]

Highbranched styrene-butyl acrylate copolymer (B-1): produced by adding 95 parts by styrene monomer, 5 parts of butyl acrylate, 10 parts of toluene, 200 ppm (monomer ratio) of tert-butyl peroxybenzoate, and 500 ppm (monomer ratio) of the highbranched macromonomer (Mm-1) produced in Reference Example 1, reacting these in a stirring-type reaction tank at 120°C for 1.5 hours and at 130°C to 170°C for 3.5 hours, removing the unreacted monomers and toluene at 230°C and a vacuum degree of 70 to 30 Torr, and purifying the residue.

[0095]

Highbranched styrene-butyl acrylate copolymer (B-2): the same as (B-1) except that the macromonomer was changed to Mm-2 produced in Reference Example 2.

[0096]

Highbranched styrene-butyl acrylate copolymer (B-3): the same as (B-1) except that the macromonomer was changed to Mm-3 produced in Reference Example 3.

[0097]

Highbranched styrene-butyl acrylate copolymer (B-4): the same as (B-1) except that the macromonomer was changed

to Mm-4 produced in Reference Example 4.

[0098]

Highbranched styrene-butyl acrylate copolymer (B-5):
the same as (B-1) except that the macromonomer was changed
to Mm-5 produced in Reference Example 5.

[0099]

Highbranched styrene-butyl acrylate copolymer (B-6):
the same as (B-1) except that the macromonomer was changed
to Mm-6 produced in Reference Example 6.

[0100]

Highbranched styrene-butyl acrylate copolymer (B-7):
the same as (B-1) except that the macromonomer was changed
to Mm-7 produced in Reference Example 7.

[0101]

Highbranched styrene-butyl acrylate copolymer (B-8):
the same as (B-1) except that the macromonomer was changed
to Mm-8 produced in Reference Example 8.

[0102]

Straight-chain styrene-butyl acrylate copolymer (B')
used for comparison: produced by adding 95 parts by styrene
monomer, 5 parts of butyl acrylate, 10 parts of toluene, and
200 ppm (monomer ratio) of tert-butyl peroxybenzoate,
reacting these in a stirring-type reaction tank at 120°C for
1.5 hours and at 130°C to 170°C for 3.5 hours, removing the
unreacted monomers and toluene at 230°C and a vacuum degree

of 70 to 30 Torr, and purifying the residue.

[0103]

The polylactic acid (C) used had a flowability of 10 g/10 min (190°C, 21.2 N), D-isomer: 1.4 mol%, weight-average molecular weight: 180,000).

[0104]

Endothermic decomposition-type sodium bicarbonate-based foaming agent "Serubon SC-K" manufactured by Eiwa Chemical Industry Co., Ltd. was used as a foaming agent.

[0105]

General-purpose talc was used as a foam-nucleating agent.

[0106]

EXAMPLE 1

The impact-resistant styrene-based resin (A-1), the highbranched styrene-acrylic acid ester copolymer (B-1), the polylactic acid (C), the sodium bicarbonate-based foaming agent, and talc at 65/25/10/1.0/2 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then foamed by a T-die with a tip set to 140°C, thereby producing a sheet (foaming magnification: 2.0 times) of 1.5 mm.

[0107]

EXAMPLE 2

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example

1 except that the impact-resistant styrene-based resin was changed to (A-2).

[0108]

EXAMPLE 3

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the impact-resistant styrene-based resin was changed to (A-3).

[0109]

EXAMPLE 4

The impact-resistant styrene-based resin (A-1), the highbranched styrene-acrylic acid ester copolymer (B-1), the polylactic acid (C), the sodium bicarbonate-based foaming agent, and talc at 75/20/5/1.0/2 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then foamed by a T-die with a tip set to 140°C, thereby producing a sheet (foaming magnification: 2.3 times) of 1.5 mm.

[0110]

EXAMPLE 5

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-2).

[0111]

EXAMPLE 6

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-3).

[0112]

EXAMPLE 7

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-4).

[0113]

EXAMPLE 8

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-5).

[0114]

EXAMPLE 9

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-6).

[0115]

EXAMPLE 10

A foamed sheet (foaming magnification: 2.0 times) of

1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-7).

[0116]

EXAMPLE 11

A foamed sheet (foaming magnification: 2.0 times) of 1.5 mm was produced under the same conditions as in Example 1 except that the highbranched styrene-acrylic acid ester copolymer was changed to (B-8).

[0117]

COMPARATIVE EXAMPLE 1

The impact-resistant styrene-based resin (A-1), the polylactic acid (C), the sodium bicarbonate-based foaming agent, and talc at 90/10/2/2 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then foamed by a T-die with a tip set to 140°C, thereby producing a sheet (foaming magnification: 1.9 times) of 1.5 mm.

[0118]

COMPARATIVE EXAMPLE 2

The impact-resistant styrene-based resin (A-1) and the sodium bicarbonate-based foaming agent at 100/2 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then foamed by a T-die with a tip set to 140°C, thereby producing a sheet (foaming magnification: 2.8 times) of 1.5 mm.

[0119]

COMPARATIVE EXAMPLE 3

The impact-resistant styrene-based resin (A-1) and the polylactic acid (C) at 95/5 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then formed into a sheet of 1.5 mm by a T-die.

[0120]

COMPARATIVE EXAMPLE 4

The impact-resistant styrene-based resin (A-1), the straight-chain styrene-acrylic acid ester copolymer (B'), the polylactic acid (C), the sodium bicarbonate-based foaming agent, and talc at 65/25/10/1.0/2 parts were dry-blended, melt-kneaded at 220°C by using a uniaxial extruder, and then foamed by a T-die with a tip set to 140°C, thereby producing a sheet (foaming magnification: 2.0 times) of 1.5 mm.

[0121]

Evaluation results are shown in Tables 1 and 2.

[0122]

[Table 1]

Styrene-butyl acrylate copolymer	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B'
Mw (10,000)	34	32	32	32	34	32	34	30	30
MFR (g/10 min)	4.8	4.9	4.9	4.9	4.8	4.9	4.8	5.2	5.2

[0123]

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5
A	A-1	A-2	A-3	A-1	A-1
B	B-1	B-1	B-1	B-1	B-2
A/B/C (parts)	65/25/10	65/25/10	65/25/10	70/20/5	65/25/10
Foaming agent (parts)	1.0	1.0	1.0	1.0	1.0
Talc (parts)	2	2	2	2	2
Oil resistance (min)	100	100	90	85	100
Secondary moldability	A	A	A	A	A
Heat resistance	A	A	A	A	A

[0124]

[Table 3]

	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
A	A-1	A-1	A-1	A-1	A-1	A-1
B	B-3	B-4	B-5	B-6	B-7	B-8
A/B/C (parts)	65/25/10	65/25/10	65/25/10	65/25/10	65/25/10	65/25/10
Foaming agent (parts)	1.0	1.0	1.0	1.0	1.0	1.0
Talc (parts)	2	2	2	2	2	2
Oil resistance (min)	100	100	100	100	100	70
Secondary moldability	A	A	A	A	A	A
Heat resistance	A	A	A	A	A	A

[0125]

[Table 4]

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
A	A-1	A-1	A-1	A-1
B	-	-	B-5	B'
A/B/C (parts)	90/0/10	100/0/0	95/0/5	65/25/10
Foaming agent (parts)	2.0	2.0	0	1.0
Talc (parts)	2	0	0	2
Oil resistance (min)	80	20	30	100
Secondary moldability	B	A	B	B
Heat resistance	A	A	A	A

CLAIMS

[Claim 1]

A styrene-based foamed sheet produced by foaming a styrene-based resin composition containing an impact-resistant styrene-based resin (A), a highbranched styrene-acrylic acid ester copolymer (B), and polylactic acid (C), the highbranched styrene-acrylic acid ester copolymer (B) being produced by copolymerizing a highbranched macromonomer (b1) having a plurality of branches and a plurality of polymerizable double bonds, a styrene-based monomer (b2), and an acrylic acid ester (b3).

[Claim 2]

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

[Claim 3]

The styrene-based foamed sheet according to Claim 2, wherein the highbranched styrene-acrylic acid ester copolymer (B) has a weight-average molecular weight within a range of 150,000 to 700,000 determined by GPC-MALLS.

[Claim 4]

The styrene-based foamed sheet according to any one of Claims 1 to 3, wherein the impact-resistant styrene-based resin (A) is produced by graft copolymerization of a rubber polymer to a continuous phase composed of a styrene homopolymer.

[Claim 5]

The styrene-based foamed sheet according to any one of Claims 1 to 4, wherein the use ratio of the styrene-based monomer (b2) to the acrylic acid ester (b3) in the highbranched styrene-acrylic acid ester copolymer (B) is within a range of 95/5 to 85/15 in terms of mass ratio of styrene-based monomer (b2)/acrylic acid ester (b3).

[Claim 6]

The styrene-based foamed sheet according to any one of Claims 1 to 5, wherein the acrylic acid ester of the highbranched styrene-acrylic acid ester copolymer (B) is butyl acrylate.

[Claim 7]

The styrene-based foamed sheet according to Claim 4, wherein the content of the rubber polymer in the impact-resistant styrene-based resin (A) is within a range of 1.5% to 15% by mass.

[Claim 8]

The styrene-based foamed sheet according to any one of Claims 1 to 7, wherein in foam molding, the magnification is

1.2 to 3.0.

[Claim 9]

The styrene-based foamed sheet according to Claim 8,
wherein the foaming is chemical foaming.

[Claim 10]

A molded product produced by a thermoforming method for
molding the styrene-based foamed sheet according to any one
of Claims 1 to 9.

[Claim 11]

The molded product according to Claim 10, wherein the
molded product is used for food packaging.