

DESCRIPTION

TITLE OF INVENTION: RESIN FOAM

TECHNICAL FIELD

[0001]

The present disclosure relates to a resin foam.

This application is based on and claims the benefit of priority of Japanese Patent Application No. 2021-206942 filed on December 21, 2021, the entire contents of which are incorporated herein by reference.

BACKGROUND ART

[0002]

Patent Literature 1 describes a polyolefin-based resin open-cell foam. The polyolefin-based resin open-cell foam is obtained by heating, under normal pressure, a molded body obtained by adding a resin composition in which 80 parts by weight of an ethylene-vinyl acetate copolymer, 20 parts by weight of low-density polyethylene, 0.6 parts by weight of dicumyl peroxide, 20 parts by weight of an azodicarbonamide-based foaming agent, 0.5 parts by weight of a silicone-based surfactant, and 10 parts by weight of talc as a foam breaker are blended, to be crosslinked and foamed.

CITATIONS LIST

PATENT LITERATURE

[0003]

Patent Literature 1: JP 10-310654 A

SUMMARY OF INVENTION

TECHNICAL PROBLEMS

[0004]

However, conventional resin foams have a poor foam-breaking property and insufficient flexibility. In addition, it is required to refine cells of the resin foam and to improve various properties such as sealability depending on the use of the resin foam.

[0005]

The present disclosure has been made in view of the above circumstances, and an object of the present disclosure is to improve the foam-breaking property of a resin foam and to realize refinement of cells. The present disclosure can be implemented in the following forms.

SOLUTIONS TO PROBLEMS

[0006]

A resin foam obtained by foaming a resin composition containing: a polyolefin-based resin containing at least an ethylene-vinyl acetate copolymer; and a petroleum resin and/or a styrene-based resin.

ADVANTAGEOUS EFFECTS OF INVENTION

[0007]

The resin foam of the present disclosure has a good foam-breaking property and has fine cells.

BRIEF DESCRIPTION OF DRAWINGS

[0008]

Fig. 1 is a plan view showing a sample for measuring a water sealing property.

Fig. 2 is a view showing a method for measuring a water

sealing property.

DESCRIPTION OF EMBODIMENTS

[0009]

Desirable examples of the present disclosure will now be described.

- A resin foam wherein the petroleum resin and/or the styrene-based resin is contained in an amount of 2.0 parts by mass or more and 20 parts by mass or less based on 100 parts by mass of the total of the polyolefin-based resin.

- A resin foam wherein the resin composition contains a silicone resin.

- A resin foam wherein the silicone resin is contained in an amount of more than 0 parts by mass and 10 parts by mass or less based on 100 parts by mass of the total of the polyolefin-based resin.

- A resin foam wherein the number of cells based on JIS K6767 is 50 cells/25 mm or more.

[0010]

Hereinafter, the present disclosure will be described in detail. In the present specification, the description using "to" for the numerical range includes the lower limit and the upper limit unless otherwise specified. For example, the expression "10 to 20" includes both the lower limit "10" and the upper limit "20". That is, the expression "10 to 20" has the same meaning as "10 or more and 20 or less".

[0011]

1. Resin foam

The resin foam of the present disclosure is formed by foaming a resin composition containing: a polyolefin-based resin containing at least an ethylene-vinyl acetate copolymer; and a petroleum resin and/or a styrene-based resin.

[0012]

The resin composition preferably contains a polyolefin-based resin, a petroleum resin and/or a styrene-based resin, and a silicone resin. Further, the resin composition may contain a foaming agent and a crosslinking agent (vulcanizing agent).

Each component of the composition will be described.

[0013]

(1) Polyolefin-based resin

The polyolefin-based resin is not particularly limited except that it contains an ethylene-vinyl acetate copolymer (EVA). The polyolefin-based resin may contain only EVA, but preferably contains EVA and a polyolefin-based resin other than EVA.

[0014]

The ethylene-vinyl acetate copolymer is a polymer containing a structural unit derived from ethylene and a structural unit derived from vinyl acetate in the molecule.

The content of vinyl acetate in EVA is not particularly limited. From the viewpoint of improving flexibility, the content of vinyl acetate is preferably 5 mass% or more, and more preferably 10 mass% or more, when the mass of EVA is 100

mass%. From the viewpoint of preventing excessive crosslinking, the content of vinyl acetate is preferably 40 mass% or less, and more preferably 30 mass% or less. From these viewpoints, the content of the vinyl acetate is preferably 5 mass% or more and 40 mass% or less, and more preferably 10 mass% or more and 30 mass% or less. The content of vinyl acetate is in accordance with JIS K6924-1.

[0015]

The melt flow rate (MFR) of EVA is not particularly limited. From the viewpoint of moldability, the MFR of EVA is, as a value measured at 190°C under a load of 2.16 kg in accordance with JIS K6924-1, preferably 0.1 g/10 min to 20 g/10 min, more preferably 0.3 g/10 min to 10 g/10 min, and still more preferably 0.5 g/10 min to 5.0 g/10 min.

[0016]

The content of EVA is more than 0 parts by mass, preferably 40 parts by mass or more, and more preferably 60 parts by mass or more, when the total amount of the polyolefin-based resin is 100 parts by mass, from the viewpoint of flexibility in the foam breaking step. From the viewpoint of preventing excessive crosslinking, the content of the EVA is 100 parts by mass or less, preferably 90 parts by mass or less, and more preferably 80 parts by mass or less. From these viewpoints, the content of the EVA is more than 0 parts by mass and 100 parts by mass or less, preferably 40 parts by mass or more and 90 parts by mass or less, and more preferably 60 parts by mass or more and 80

parts by mass or less.

[0017]

Examples of the polyolefin-based resin other than EVA include polyethylene-based resins (excluding EVA), polypropylene-based resins, and mixtures thereof. The polyolefin-based resin other than EVA may be blended as a diluent resin of a masterbatch. Examples of the masterbatch include silicone masterbatches containing a silicone resin, and foaming agent masterbatches.

[0018]

Examples of the polyethylene-based resin (excluding EVA) include low-density polyethylene (LDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), an ethylene-propylene copolymer, an ethylene-1-butene copolymer, an ethylene-propylene-1-butene copolymer, an ethylene-(4-methyl-1-pentene) copolymer, and an ethylene-acrylic acid ester copolymer. These polyethylene-based resins may be used alone, or may be used in combination of two or more thereof.

[0019]

The low-density polyethylene is usually formed by randomly branching and bonding repeating units of ethylene. From the viewpoint of moldability, the low-density polyethylene preferably has a melt flow rate (MFR) of 0.1 g/10 min to 20 g/10 min, more preferably 0.3 g/10 min to 10 g/10 min, and still more preferably 0.5 g/10 min to 5.0 g/10 min, as measured at 190°C under a load of 2.16 kgf in

accordance with JIS K7210-1.

[0020]

The linear low-density polyethylene is a copolymer of ethylene and α -olefin having no long chain branch. Examples of the α -olefin include propylene, 1-butene, 1-heptene, 1-hexene, 1-octene, and 4-methyl-1-pentene.

[0021]

The polypropylene-based resin is a polymer containing a structural unit derived from propylene in one molecule, and is obtained by polymerizing a monomer component containing propylene. The polypropylene-based resin may be a propylene homopolymer or a copolymer of propylene and an olefin other than propylene (excluding ethylene). The polypropylene-based resin may be used alone, or may be used in combination of two or more thereof.

[0022]

The polyolefin-based resin preferably contains EVA and a polyethylene-based resin (excluding EVA), and more preferably contains EVA and low-density polyethylene, from the viewpoint of adjusting the degree of crosslinking and melt viscosity for obtaining a good foam and preventing sagging after foam breakage.

The content of the low-density polyethylene is preferably 0 parts by mass or more and 50 parts by mass or less, more preferably 5 parts by mass or more and 40 parts by mass or less, and still more preferably 10 parts by mass or more and 35 parts by mass or less, when the total of the

polyolefin-based resins is 100 parts by mass.

[0023]

(2) Petroleum resin

The petroleum resin is obtained by polymerizing a fraction containing an unsaturated hydrocarbon monomer generated as a by-product through thermal decomposition of petroleum naphtha or the like. Examples of the petroleum resin include aliphatic petroleum resins (C5 petroleum resins), aromatic petroleum resins (C9 petroleum resins), aliphatic/aromatic petroleum resins (C5/C9 petroleum resins), and alicyclic petroleum resins (hydrogenated petroleum resins). The aliphatic petroleum resin (C5 petroleum resin) is a synthetic resin obtained by polymerizing a refined component of a C5 fraction of petroleum naphtha crack oil. The aromatic petroleum resin (C9 petroleum resin) is a synthetic resin obtained by polymerizing a refined component of a C9 fraction of petroleum naphtha crack oil. The aliphatic/aromatic petroleum resin (C5/C9 petroleum resin) is a synthetic resin obtained by copolymerizing a raw material obtained by blending the C5 fraction and the C9 fraction.

The petroleum resin is particularly preferably a C9 hydrogenated petroleum resin from the viewpoint of compatibility with the polyolefin-based resin.

[0024]

The petroleum resin is preferably a hydrogenated petroleum resin from the viewpoint of odor, hue, thermal stability, weather resistance, and compatibility with the

polyolefin-based resin. The hydrogenated petroleum resin is a resin in which a hydrogen atom is added to an unsaturated double bond present in the petroleum resin. As the hydrogenated petroleum resin, either a completely hydrogenated petroleum resin having a hydrogenation rate of 90% or more or a partially hydrogenated petroleum resin having a hydrogenation rate of less than 90% can be used.

The hydrogenation rate of the petroleum resin is not particularly limited. From the viewpoint of suitably refining the cells, the hydrogenation rate of the petroleum resin is preferably 5% or more, more preferably 10% or more, still more preferably 25% or more, and may be 40% or more. The upper limit of the hydrogenation rate of the petroleum resin is not particularly limited, and may be 100%, 90% or less, 80% or less, or 70% or less.

[0025]

Examples of commercially available products of the C9 hydrogenated petroleum resin include ARKON P-90, ARKON P-100, ARKON P-115, ARKON P-125, ARKON P-140, ARKON M-90, ARKON M-100, ARKON M-115, and ARKON M-135 (manufactured by Arakawa Chemical Industries, Ltd.). Examples of commercially available products of the C5 hydrogenated petroleum resin include Eastotac C115W (manufactured by Eastman Chemical Company). Examples of commercially available products of the C5/C9 hydrogenated petroleum resin include dicyclopentadiene/aromatic copolymer-based hydrogenated petroleum resins such as I-MARV S-100, I-MARV S-110, I-MARV

P-100, I-MARV P-125, and I-MARV P-140 (manufactured by Idemitsu Kosan Co., Ltd.). Examples of commercially available products of the C5/C9 unhydrogenated petroleum resin include Petrotack 70 (manufactured by Tosoh Corporation).

The number at the end of the product name is a catalog value indicating the softening point (°C) of the petroleum resin. From the viewpoint of handleability, the softening point of the petroleum resin can be, for example, 70°C or higher, 80°C or higher, or 90°C or higher, and is preferably higher than 90°C, more preferably 100°C or higher, or 110°C or higher. The upper limit of the softening point is not particularly limited, but may be, for example, 140°C or lower in view of easy availability. The difference in softening point does not significantly affect the properties of the resin foam, but a petroleum resin having a low softening point may cause blocking or the like in which a powdery material becomes a lump during transportation, storage, or the like. In this regard, when the softening point is within the above range, handling of the petroleum resin is easy.

The petroleum resin may be used alone, or may be used in combination of two or more thereof.

[0026]

(3) Styrene-based resin

The styrene-based resin can be obtained by addition polymerization of one type or two or more types of styrene-based monomers. The addition polymerization reaction can be

performed according to a known method. The addition polymerization can be performed by, for example, by a method of performing solution polymerization using a living anionic polymerization catalyst, a method using a cationic polymerization catalyst, a method using a radical polymerization initiator, or the like. Examples of the styrene-based monomer include styrene, α -methylstyrene, β -methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, and 4-phenylstyrene.

The styrene-based resin may be used alone, or may be used in combination of two or more thereof.

[0027]

The styrene-based resin is preferably a hydrogenated styrene-based resin from the viewpoint of, for example, compatibility with the polyolefin-based resin. The hydrogenated styrene-based resin is obtained by hydrogenating a styrene-based resin to change at least a part of an aromatic ring to an alicyclic ring.

[0028]

The hydrogenated styrene-based resin can be obtained by hydrogenating at least a part of an aromatic ring derived from a styrene-based monomer in the styrene-based resin. The hydrogenation method is conventionally known and is not particularly limited.

For example, hydrogenation is performed by bringing hydrogen into contact with a solution in which the styrene-based resin is dissolved in a solvent in the presence of a

known hydrogenation catalyst by a method such as blowing hydrogen. Examples of the hydrogenation catalyst include homogeneous catalysts composed of combinations of transition metal compounds/alkyl metal compounds such as cobalt acetate/triethylaluminum, nickel acetylacetonate/triisobutylaluminum, titanocene dichloride/n-butyllithium, zirconocene dichloride/sec-butyllithium, and tetrabutoxytitanate/dimethylmagnesium; heterogeneous metal catalysts such as nickel, palladium, and platinum; heterogeneous solid-supported catalysts such as nickel/silica, nickel/diatomaceous earth, nickel/alumina, palladium/carbon, palladium/silica, palladium/diatomaceous earth, and palladium/alumina, in which a metal catalyst is supported on the support.

[0029]

The hydrogenation rate of the hydrogenated styrene-based resin is not particularly limited. From the viewpoint of suitably refining the cells, the hydrogenation rate of the hydrogenated styrene-based resin is preferably 5% or more, more preferably 10% or more, still more preferably 25% or more, and may be 40% or more. The upper limit of the hydrogenation rate of the hydrogenated styrene-based resin is not particularly limited, and may be 100%, or may be 95% or less, 90% or less, 80% or less, or 70% or less.

[0030]

Here, the hydrogenation rate of the hydrogenated styrene-based resin is a value calculated from the peak

height of absorbance derived from the styrene compound measured by IR (infrared spectrophotometer) by the following formula.

$$\text{Hydrogenation rate (\%)} = \{(C - D)/C\} \times 100$$

C: Absorbance peak height derived from aromatic ring before hydrogenation

D: Absorbance peak height derived from aromatic ring after hydrogenation

[0031]

The molecular weight of the styrene-based resin is not particularly limited. The molecular weight of the styrene-based resin is, as a weight average molecular weight (Mw) in terms of polystyrene by gel permeation chromatography (GPC), preferably 500 to 10,000, more preferably 800 to 5,000, and still more preferably 1,000 to 4,000.

Examples of commercially available products of the styrene-based resin include, as a hydrogenated styrene-based resin, YS Resin SG-110, YS Resin SM-100, and YS Resin SS-115 (manufactured by Yasuhara Chemical Co., Ltd.). Examples of commercially available products of the styrene-based resin include, as an unhydrogenated styrene-based resin, YS Resin SX-100 (manufactured by Yasuhara Chemical Co., Ltd.).

[0032]

(4) Content of petroleum resin and/or styrene-based resin

The content of the petroleum resin and/or the styrene-based resin is preferably 2.0 parts by mass or more, more

preferably 3.0 parts by mass or more, and still more preferably 4.0 parts by mass or more, based on 100 parts by mass of the total of the polyolefin-based resin, from the viewpoint of improvement in the foam-breaking property and refinement of the cells. From the viewpoint of suppressing deterioration in physical properties such as loss of restoration of the resin foam due to excessive foam breakage, the content of the petroleum resin and/or styrene-based resin is preferably 20 parts by mass or less, more preferably 15 parts by mass or less, and still more preferably 12 parts by mass or less. From these viewpoints, the content of the petroleum resin and/or the styrene-based resin is preferably 2.0 parts by mass or more and 20 parts by mass or less, more preferably 3.0 parts by mass or more and 15 parts by mass or less, and still more preferably 4.0 parts by mass or more and 12 parts by mass or less. Further, even when the content of the petroleum resin and/or the styrene-based resin is 8 parts by mass or less, or 6 parts by mass or less, it is possible to achieve improvement in the foam-breaking property and refinement of the cells.

When the resin composition contains only one of a petroleum resin and a styrene-based resin, the content of the petroleum resin and/or the styrene-based resin means the content of the one resin. When the resin composition contains both a petroleum resin and a styrene-based resin, the content of the petroleum resin and/or the styrene-based resin means the total content of the petroleum resin and the

styrene-based resin.

[0033]

(5) Silicone resin

The silicone resin is an optional component. As the silicone resin, for example, polyorganosiloxane or the like can be suitably used. Here, polyorganosiloxane has a siloxane bond as a main chain and an organic group in a side chain. Examples of the organic group include a methyl group, a vinyl group, an ethyl group, a propyl group, and a phenyl group.

[0034]

Specific examples of the polyorganosiloxane include dimethylpolysiloxane, methylethylpolysiloxane, methyloctylpolysiloxane, methylvinylpolysiloxane, methylphenylpolysiloxane, and methyl(3,3,3-trifluoropropyl)polysiloxane.

[0035]

The silicone resin can be used in the form of silicone gum, silicone powder, silicone oil, or silicone resin. Among these, from the viewpoint that blooming is less likely to occur, it is preferable to use the silicone resin in the form of silicone gum.

[0036]

The content of the silicone resin is preferably more than 0 part by mass, more preferably 1.0 parts by mass or more, and still more preferably 1.5 parts by mass or more, based on 100 parts by mass of the total of the polyolefin-

based resin, from the viewpoint of improving a water sealing property by imparting water repellency. From the viewpoint of dispersibility in the polyolefin-based resin, the content of the silicone resin is preferably 10 parts by mass or less, more preferably 7 parts by mass or less, and still more preferably 5 parts by mass or less. From these viewpoints, the content of the silicone resin is preferably more than 0 parts by mass and 10 parts by mass or less, more preferably 1.0 parts by mass or more and 7 parts by mass or less, and still more preferably 1.5 parts by mass or more and 5 parts by mass or less.

[0037]

(6) Foaming agent

The foaming agent is not particularly limited, but is preferably a thermal decomposition type foaming agent that is decomposed by heat to generate a gas. As the thermal decomposition type foaming agent, an organic foaming agent or an inorganic foaming agent can be used.

[0038]

Examples of the organic foaming agent include azodicarbonamide (ADCA), barium azodicarboxylate, azobisisobutyronitrile (AIBN), azocyclohexylnitrile, N,N'-dinitrosopentamethylenetetramine, 4,4'-oxybisbenzenesulfonylhydrazide, and toluenesulfonylsemicarbazide.

[0039]

Examples of the inorganic foaming agent include

ammonium carbonate, sodium carbonate, ammonium hydrogen carbonate, sodium hydrogen carbonate, sodium nitrite, ammonium nitrite, sodium borohydride, and anhydrous monosodium citrate.

[0040]

The foaming agent may be used alone, or may be used in combination of two or more thereof. Among them, azo compounds such as azodicarbonamide, barium azodicarboxylate, and azobisisobutyronitrile, and nitroso compounds such as N,N'-dinitrosopentamethylenetetramine are preferable, and azodicarbonamide (ADCA) is particularly preferable, because fine cells can be formed.

[0041]

The foaming agent is preferably 5 to 35 parts by mass, more preferably 10 to 30 parts by mass, and still more preferably 15 to 25 parts by mass based on 100 parts by mass of the total of the polyolefin-based resin.

[0042]

(7) Crosslinking agent

The crosslinking agent is not particularly limited. Examples of the crosslinking agent include organic peroxides such as dicumyl peroxide (DCP), 2,5-dimethyl-2,5-bis-tertiary butyl peroxyhexane, and 1,3-bis-tertiary peroxyisopropylbenzene.

[0043]

(8) Other components

The resin composition may contain, as necessary,

additives such as a filler (calcium carbonate or the like), a foaming aid (zinc stearate, urea-based foaming aid, and the like), a crosslinking aid, an antioxidant, a pigment, a plasticizer, thermally expandable particles, and a function imparting agent (for example, flame retardant). These additives may be used alone, or may be used in combination of two or more thereof.

The composition may also contain a polymer (hereinafter, also referred to as other polymers) such as a modifier other than the above-described polymers as long as the effect of the present disclosure is not significantly inhibited.

[0044]

2. Configuration of resin foam

The cell structure of the resin foam is not particularly limited. The resin foam preferably has an open-cell structure. As described later, the resin foam having an open-cell structure can be obtained by rupturing the cell membrane to interconnect cells of the resin foam. When the resin foam has an open-cell structure, the following physical properties of the resin foam is measured using a sample that has undergone a foam breaking step described later. The conditions of the foam breaking step can be appropriately changed according to the required physical properties, but the following physical properties of the resin foam are, for example, values measured using a sample that has passed through rolls 10 times in the foam breaking step.

[0045]

(1) Number of cells

In the resin foam of the present disclosure, the number of cells, as measured based on the procedure described in JIS K6767:1999 Appendix A (definition) Cell Counting Procedure, is preferably 50 cells/25 mm or more, more preferably 60 cells/25 mm or more, and still more preferably 70 cells/25 mm or more. The upper limit of the number of cells is not particularly limited, but may be, for example, 100 cells/25 mm or less, 90 cells/25 mm or less, or 85 cells/25 mm or less.

In the present disclosure, the cell means a pore portion in the foam. The number of cells is the number of cells per 25 mm of the test piece counted based on JIS K6767:1999.

[0046]

(2) Density

The density of the resin foam is preferably 20 kg/m³ or more and 100 kg/m³ or less, more preferably 25 kg/m³ or more and 50 kg/m³ or less, and still more preferably 30 kg/m³ or more and 40 kg/m³ or less. The density is an apparent density measured according to JIS K7222:2005. By setting the density within the above range, the weight of the resin foam can be reduced.

As shown in the following formula, the expansion ratio can be calculated as the reciprocal of the density.

$$\text{Expansion ratio} = 1,000/A \quad A: \text{density (kg/m}^3\text{)}$$

The expansion ratio of the resin foam is preferably 10 times to 50 times, more preferably 20 times to 40 times, and still more preferably 25 times to 35 times.

[0047]

(3) Compressive stress 50%

The compressive stress of the resin foam is preferably 10 kPa or less, more preferably 8 kPa or less, and still more preferably 5.5 kPa or less when measured in accordance with the test method of "compressive stress-strain" in JIS K6767:1999 (50% compression, corresponding to ISO 3386-1). The lower limit of the compressive stress of the resin foam is not particularly limited, but is usually 0.1 kPa or more.

The compressive stress of the resin foam can be adjusted, for example, by changing the blending ratio of the petroleum resin and/or the styrene-based resin in the resin composition, the degree of interconnection of cells, and the like.

[0048]

(4) Compression set

The compression set of the resin foam is preferably 5.0% or less, more preferably 3.0% or less, and still more preferably 2.5% or less when measured in accordance with the test method of "compression set" in JIS K6767:1999 (thickness measurement 24 hours after completion of compression, corresponding to ISO 1856). The lower limit of the compression set of the resin foam is not particularly limited, but is usually 0.1% or more.

[0049]

(5) Gel fraction

The gel fraction of the resin foam is preferably 30% or more, more preferably 50% or more, and still more preferably 70% or more. The upper limit of the gel fraction is 100% or less, and may be, for example, 95% or less, or 90% or less. The gel fraction is measured in accordance with JIS K6796. A higher numerical value of the gel fraction indicates a higher degree of crosslinking of the resin foam.

The gel fraction can be adjusted by changing the type of crosslinking agent, the blending ratio, the presence or absence of electron beam crosslinking, the conditions of electron beam crosslinking, and the like.

[0050]

(6) Water sealing property and applications

The resin foam is suitable as a water sealing material. When the resin foam is used as a water sealing material, the resin foam is formed by punching or the like to have a thickness and a shape (for example, a string shape) corresponding to its application, and used. The holding time for 100 mmAq water pressure of the resin foam described later is preferably 30 minutes or more, more preferably 9 hours or more, and still more preferably 24 hours or more. As for the holding time for 100 mmAq water pressure, a sample 1 for measuring a water sealing property, which is prepared by punching a water sealing material having a thickness of 10 mm into a U-shape with the dimensions shown in Fig. 1, is

sandwiched between two acrylic resin plates 2 in a compressed state at a predetermined compression ratio (for example, 50%, 60%, 70%) as shown in Fig. 2, and in this state, water W is injected into the U-shaped test sample 1 so as to have a water pressure of 100 mAq. The holding time for 100 mmAq water pressure is a time during which the water pressure of 100 mmAq is held.

The application of the resin foam is not limited to the water sealing material. The resin foam can be widely used for various sealing materials, cushioning materials, heat insulating materials, adsorbents, building members, automobile members, daily materials, and the like.

[0051]

3. Method for producing resin foam

The method for producing the resin foam is not particularly limited, but for example, a method in which a foaming agent is added to a polyolefin-based resin, a crosslinking agent or other additives are optionally added as necessary and mixed, and then foam molding is performed, can be adopted. Preferably, the method for producing a polyolefin-based resin foam may be any of a two-stage block foaming method, a one-stage block foaming method, a long foaming method using chemical crosslinking, and a long foaming method using electron beam crosslinking as described below. Among them, the block foaming method is preferable in that a resin foam having a relatively large thickness can be produced, and the compression ratio can be increased in the

foam breaking step described later due to the large thickness, and the two-stage block foaming method is more preferable.

[0052]

<Two-stage block foaming method>

The two-stage block foaming method includes, for example, the following steps (1) to (4).

(1) Kneading step

A polyolefin-based resin, a petroleum resin and/or a styrene-based resin, a crosslinking agent, a foaming agent, a silicone resin (optional component), an additive (optional component), and a filler and an auxiliary agent needed as appropriate are melt-kneaded at a temperature equal to or lower than the decomposition temperature of the foaming agent by a kneading apparatus such as an extruder, a Banbury mixer, a kneader, or a roll, thereby obtaining a foamable resin composition.

(2) Primary foaming step

The foamable resin composition obtained in the kneading step is filled in a molding space of a primary mold, and heated under pressure. As a result, a part of the crosslinking agent or a part of the crosslinking agent and the foaming agent are decomposed. Thereafter, the pressure is removed and the foamable resin composition intermediate is taken out. The heating temperature is usually determined to be 130 to 150°C, and the heating time is usually determined to be in the range of 25 to 50 minutes.

(3) Secondary foaming step

The foamable resin composition intermediate obtained in the primary foaming step is disposed in a molding space of a secondary mold, heated under normal pressure to be secondarily foamed, and then a resin foam is taken out from the secondary mold.

(4) Foam breaking step

The resin foam obtained in the secondary foaming step is subjected to a compression process of causing the resin foam to pass between two rolls rotating in different directions, to obtain an open-cell resin foam.

This step is a step of performing a compression process of causing the resin foam to pass between two rolls rotating in different directions to thereby rupture the cell membrane and interconnect cells of the resin foam. Here, the compression conditions during the compression process (compression ratio, circumferential speed ratio between rolls) and the number of compression processes can be appropriately set according to the degree of interconnection of cells. For example, the compression process is preferably repeated a plurality of times.

[0053]

<One-stage block foaming method>

The one-stage block foaming method includes, for example, the following steps (1) to (3).

(1) Kneading step

A polyolefin-based resin, a petroleum resin and/or a

styrene-based resin, a crosslinking agent, a foaming agent, a silicone resin (optional component), an additive (optional component), and a filler and an auxiliary agent needed as appropriate are melt-kneaded at a temperature equal to or lower than the decomposition temperature of the foaming agent by a kneading apparatus such as an extruder, a Banbury mixer, a kneader, or a roll, thereby obtaining a foamable resin composition.

(2) Foaming step

The foamable resin composition obtained in the kneading step is filled in a mold, sealed, and heated (heated at a temperature equal to or higher than the decomposition temperature of the foaming agent and the crosslinking agent) for a predetermined time in a pressurized state to promote crosslinking of the crosslinking agent and decomposition of the foaming agent, and then the mold is opened and the pressure is removed, thereby obtaining a resin foam.

(3) Foam breaking step

The resin foam obtained in the foaming step is subjected to a compression process of causing the resin foam to pass between two rolls rotating in different directions, to obtain an open-cell resin foam. For details, the description of the foam breaking step in the two-stage block foaming method is cited.

[0054]

<Long foaming method using chemical crosslinking>

The long foaming method includes, for example, the

following steps (1) to (3).

(1) Kneading step

A polyolefin-based resin, a petroleum resin and/or a styrene-based resin, a crosslinking agent, a foaming agent, a silicone resin (optional component), an additive (optional component), and a filler and an auxiliary agent needed as appropriate are kneaded and extruded into a sheet shape by a single-screw extruder, a twin-screw extruder, or the like, thereby extruding a foamable resin composition having a predetermined shape such as a sheet (hereinafter, referred to as a base sheet).

(2) Foaming step

The base sheet obtained in the kneading step is heated at 120 to 250°C (equal to or higher than the decomposition temperature of the foaming agent and the crosslinking agent) for 5 to 20 minutes to be foamed while being conveyed into a heating apparatus such as an oven, thereby obtaining a resin foam. It is preferable to use an apparatus in which a heating apparatus such as an oven and a conveyance apparatus are integrated, because the base sheet can be continuously processed.

(3) Foam breaking step

The resin foam obtained in the foaming step is subjected to a compression process of causing the resin foam to pass between two rolls rotating in different directions, to obtain an open-cell resin foam. For details, the description of the foam breaking step in the two-stage block

foaming method is cited.

[0055]

<Long foaming method using electron beam crosslinking>

The long foaming method using electron beam crosslinking includes, for example, the following steps (1) to (4).

(1) Kneading step

A polyolefin-based resin, a petroleum resin and/or a styrene-based resin, a foaming agent, a silicone resin (optional component), a crosslinking agent (optional component), an additive (optional component), and a filler and an auxiliary agent needed as appropriate are kneaded by a single-screw extruder, a twin-screw extruder, or the like, and a resin composition having a predetermined shape such as a sheet shape (hereinafter, referred to as a base sheet) is extruded. The kneading and extrusion can be collectively performed by the extruder. In order to perform uniform kneading, it is preferable to mix the components in advance and then perform extrusion.

(2) Crosslinking step

The base sheet obtained in the kneading step is crosslinked. As the crosslinking method, a method of crosslinking by ionizing radiation such as an electron beam or a γ -ray can be used. As the crosslinking method, crosslinking by electron beam irradiation (electron beam crosslinking) is preferable. This is because, according to electron beam crosslinking, it is possible to realize

refinement of the cells formed in the foam and to control the cell diameter within a predetermined range. The electron beam crosslinking can be performed using an electron beam irradiator. If necessary, chemical crosslinking may be used in combination by blending a crosslinking agent such as the organic peroxide described above.

The irradiation dose of the electron beam is preferably 4.0 Mrad to 8.0 Mrad (40 kGy to 80 kGy). When the irradiation dose is less than 4.0 Mrad, foaming may not be performed well in the foaming step described later. When the irradiation dose is more than 8.0 Mrad, crosslinking is strong and the resin becomes hard, so that there is a concern that cracking may occur during foaming. The acceleration voltage of the electron beam may be appropriately adjusted according to the thickness of the base sheet or the like, and is not particularly limited.

(3) Foaming step

The cross-linked base sheet obtained in the crosslinking step is foamed by heating at 120 to 250°C (equal to or higher than the decomposition temperature of the foaming agent and the crosslinking agent) for 5 to 20 minutes while being conveyed into a heating apparatus such as an oven, thereby obtaining a resin foam. It is preferable to use an apparatus in which a heating apparatus such as an oven and a conveyance apparatus are integrated, because the base sheet can be continuously processed.

(4) Foam breaking step

The resin foam obtained in the foaming step is subjected to a compression process of causing the resin foam to pass between two rolls rotating in different directions, to obtain an open-cell resin foam. For details, the description of the foam breaking step in the two-stage block foaming method is cited.

[0056]

4. Operation and effect of present embodiment

The resin foam of the present embodiment has a good foam-breaking property, and the cells are refined. In general, when cells are refined, the cell membrane is less likely to be ruptured, so that the foam-breaking property of the cells tends to deteriorate. In the present embodiment, however, it is presumed that since the resin composition contains a petroleum resin and/or a styrene-based resin, both of improvement in the foam-breaking property and refinement of the cells can be achieved.

More specifically, since the resin foam of the present embodiment has a good foam-breaking property, the flexibility of the resin foam can be suitably improved by having an open-cell structure. For this reason, when the resin foam is used as a sealing material, adhesion to an adherend is enhanced, thus making it possible to improve sealability.

Further, since the cells of the resin foam of the present embodiment are refined, when the resin foam is used as a sealing material, a gap is less likely to be formed between the sealing material and the adherend. Therefore,

when the resin foam is used as a sealing material, inflow of water, air, or the like from between the sealing material and the adherend can be prevented, thus making it possible to improve sealability.

[0057]

When the resin composition contains a silicone resin, the water sealing property is good. It is presumed that the silicone resin increases the water repellency of the resin foam, so that the water sealing property is improved.

EXAMPLES

[0058]

Hereinafter, more specific description will be given with reference to Examples. In Tables 1 and 2, when "*" is attached as in "Experimental Example 11*", it indicates that it is Comparative Example. Experimental Examples 1 to 10 and 13 to 20 are Examples, and Experimental Examples 11 and 12 are Comparative Examples.

[0059]

1. Production of resin foam

Resin foams of Experimental Examples were prepared at the blending ratios shown in Tables 1 and 2. In Tables 1 and 2, details of main raw materials are shown below.

[0060]

- Polyolefin-based resin 1: ethylene-vinyl acetate copolymer (EVA) (vinyl acetate content: 19 wt%, density: 941 kg/m³, MFR: 2.5 g/10 min)
- Polyolefin-based resin 2: low-density polyethylene

(LDPE) (density: 924 kg/m³, MFR: 3.0 g/10 min)

- Petroleum resin 1: C5/C9 hydrogenated petroleum resin (completely hydrogenated), I-MARV P-100 (softening point: 100°C) manufactured by Idemitsu Kosan Co., Ltd.

- Petroleum resin 2: C5/C9 hydrogenated petroleum resin (partially hydrogenated), I-MARV S-100 (softening point: 100°C) manufactured by Idemitsu Kosan Co., Ltd.

- Petroleum resin 3: C9 hydrogenated petroleum resin (completely hydrogenated), ARKON P-90 (softening point: 90°C) manufactured by Arakawa Chemical Industries, Ltd.

- Petroleum resin 4: C9 hydrogenated petroleum resin (partially hydrogenated), ARKON M-90 (softening point: 90°C) manufactured by Arakawa Chemical Industries, Ltd.

- Petroleum resin 5: C9 hydrogenated petroleum resin (partially hydrogenated), ARKON M-100 (softening point: 100°C) manufactured by Arakawa Chemical Industries, Ltd.

- Petroleum resin 6: C9 hydrogenated petroleum resin (partially hydrogenated type), ARKON M-115 (softening point: 115°C) manufactured by Arakawa Chemical Industries, Ltd.

- Styrene-based resin 1: hydrogenated styrene-based resin (C8) (partially hydrogenated), YS Resin SM-100 (softening point: 94.0°C) manufactured by Yasuhara Chemical Co., Ltd.

- Styrene-based resin 2: hydrogenated styrene-based resin (C8) (partially hydrogenated), YS Resin SG-110 (softening point: 106.5°C) manufactured by Yasuhara Chemical Co., Ltd.

- Styrene-based resin 3: styrene-based resin (C8) (unhydrogenated), YS Resin SX-100 (softening point: 101.0°C) manufactured by Yasuhara Chemical Co., Ltd.
- Petroleum resin 7: C5/C9 petroleum resin (unhydrogenated), Petrotack 70 (softening point: 70°C) manufactured by Tosoh Corporation
- Silicone masterbatch (silicone resin/polyolefin-based resin 3): masterbatch prepared by blending low-density polyethylene (LDPE) and silicone gum composed of dimethylpolysiloxane at a ratio of 1 : 1 (mass ratio), X-22-2125H, manufactured by Shin-Etsu Chemical Co., Ltd.
- Foaming agent masterbatch (ADCA/polyolefin-based resin 4): masterbatch prepared by blending azodicarbonamide (ADCA) and low-density polyethylene (LDPE) at a ratio of 3 : 2 (mass ratio)
- Filler: heavy calcium carbonate (average particle size (D50): 3.4 μm)
- Crosslinking agent: dicumyl peroxide (DCP)
- Foaming aid: foaming aid containing zinc stearate [0061]

In Tables 1 and 2, the blending ratio represents the blending ratio (parts by mass) when the total amount of the polyolefin-based resin is 100 parts by mass. As for the "silicone masterbatch", the blending ratios of the "silicone resin (silicone gum)" and the "polyolefin-based resin 3 (LDPE)" are each shown in parentheses. As for the "foaming agent masterbatch", the blending ratios of the "ADCA" and the

"polyolefin-based resin 4 (LDPE)" are each shown in parentheses.

[0062]

Raw materials were mixed at the blending ratios shown in Tables 1 and 2, and resin foams were obtained by the two-stage block foaming method described in the embodiment. In the foam breaking step, a compression process of causing a molded body to pass between two rolls rotating in different directions was performed 10 times. Each of the obtained resin foams was sliced into 10 mm, and evaluated by the evaluation method described later.

[0063]

2. Evaluation method

(1) Density (apparent density)

The density (kg/m³) was measured as an apparent density based on JIS K7222:2005.

(2) Compressive stress 50%

The compressive stress 50% (kPa) was measured in accordance with the test method of "compressive stress-strain" in JIS K6767:1999 (50% compression, corresponding to ISO 3386-1). A low compressive stress 50% is an indicator of high flexibility of the resin foam.

(3) Compression set

The compression set (%) was measured in accordance with the test method of "compression set" in JIS K6767:1999 (thickness measurement 24 hours after completion of compression, corresponding to ISO 1856).

(4) Gel fraction

The gel fraction (%) was measured in accordance with JIS K6796.

(5) Number of cells

For the number of cells, the number of cells per 25 mm of a test piece was counted based on JIS K6767:1999.

(6) Water sealing property

The holding time for 100 mmAq water pressure in the resin foam was measured by the evaluation method described in the embodiment. The compression ratio of the resin foam at the time of measurement was set to 50%. Based on the holding time for 100 mmAq water pressure, the water sealing property of the resin foam was evaluated according to the following criteria.

Pass: Holding time for 100 mmAq water pressure is 24 hours or more.

Fail: Holding time for 100 mmAq water pressure is less than 24 hours.

[0064]

[Table 1]

Table 1

		Experimental Example 1	Experimental Example 2	Experimental Example 3	Experimental Example 4	Experimental Example 5	Experimental Example 6	Experimental Example 7	Experimental Example 8	Experimental Example 9	Experimental Example 10	Experimental Example 11*	Experimental Example 12*
Blending ratio (parts by mass)	Polyolefin-based resin 1: EVA	71.00	71.00	71.00	71.00	71.00	71.00	71.00	71.00	71.00	71.00	70.00	71.00
	Polyolefin-based resin 2	17.22	17.22	19.72	19.72	19.72	19.72	19.72	19.72	17.22	17.22	19.72	16.72
	Petroleum resin 1	0.00	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Petroleum resin 2	0.00	0.00	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Petroleum resin 3	0.00	0.00	0.00	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Petroleum resin 4	5.00	10.00	0.00	0.00	0.00	2.50	5.00	10.00	0.00	0.00	0.00	0.00
	Petroleum resin 5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	0.00	0.00
	Petroleum resin 6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	0.00
	Silicone masterbatch	5.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00	5.00	5.00	0.00	6.00
	(Silicone resin)	(2.50)	(2.50)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(2.50)	(2.50)	(0.00)	(3.00)
	(Polyolefin-based resin 3)	(2.50)	(2.50)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(2.50)	(2.50)	(0.00)	(3.00)
	Foaming agent masterbatch	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20
	(ADCA)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)
	(Polyolefin-based resin 4)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)
	Filler	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80
Physical properties	Crosslinking agent	1.00	1.20	1.00	1.00	1.00	1.00	1.00	1.00	1.20	1.20	1.00	1.00
	Foaming aid	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
	Total	142.49	147.69	139.99	139.99	139.99	137.49	139.99	144.99	147.69	147.69	134.99	137.99
	Density (kg/m ³)	35	34	34	33	34	33	33	35	34	35	33	33
	Compressive stress 50% (kPa)	4.6	4.5	4.7	5.0	4.4	5.3	4.8	4.6	4.5	4.9	10.2	10.4
	Compression set (%)	2.3	2.0	2.3	2.6	2.6	3.0	2.7	2.8	2.1	2.3	3.9	3.6
	Gel fraction (%)	80.5	80.0	-	-	-	-	-	-	81.6	82.6	78.0	-
Physical properties	Number of cells (cells/25 mm)	76	80	68	62	60	56	62	63	78	77	40	42
	Water sealing property	Pass	Pass	-	-	-	-	-	-	Pass	Pass	Fail	Fail

[0065]

[Table 2]

Table 2

		Experimenta l Example 13	Experimenta l Example 14	Experimenta l Example 15	Experimenta l Example 16	Experimenta l Example 17	Experimenta l Example 18	Experimenta l Example 19	Experimenta l Example 20
Blending ratio (parts by mass)	Polyolefin- based resin 1: EVA	71.00	71.00	71.00	71.00	71.00	71.00	71.00	71.00
	Polyolefin- based resin 2	19.72	17.22	17.22	17.22	19.72	19.72	19.72	19.72
	Styrene- based resin 1	5.00	10.00	0.00	0.00	0.00	0.00	0.00	0.00
	Styrene- based resin 2	0.00	0.00	5.00	10.00	5.00	10.00	0.00	0.00
	Styrene- based resin 3	0.00	0.00	0.00	0.00	0.00	0.00	5.00	0.00
	Petroleum resin 7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.00
	Silicone masterbatch	0.00	5.00	5.00	5.00	0.00	0.00	0.00	0.00
	(Silicone resin)	(0.00)	(2.50)	(2.50)	(2.50)	(0.00)	(0.00)	(0.00)	(0.00)
	(Polyolefin -based resin 3)	(0.00)	(2.50)	(2.50)	(2.50)	(0.00)	(0.00)	(0.00)	(0.00)
	Foaming agent masterbatch	23.20	23.20	23.20	23.20	23.20	23.20	23.20	23.20
	(ADCA)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)	(13.92)
	(Polyolefin -based resin 4)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)	(9.28)
	Fillar	19.80	19.80	19.80	19.80	19.80	19.80	19.80	19.80
	Crosslinkin g agent	1.00	1.20	1.00	1.20	1.00	1.00	1.00	1.00
	Foaming aid	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Total		139.99	147.69	142.69	147.69	139.99	144.99	139.99	139.99
Physical propertie s	Density (kg/m3)	36	35	34	35	35	34	34	32
	Compressive stress 50% (kPa)	5.4	4.8	5.0	5.1	4.7	4.9	8.0	5.2
	Compression set (%)	2.6	2.5	2.0	1.8	2.2	2.2	4.4	4.1
	Gel fraction (%)	-	81.4	82.0	81.2	-	-	-	-
	Number of cells (cells/25 mm)	64	78	78	80	66	68	51	58
	Water sealing property	-	Pass	Pass	Pass	-	-	-	-

[0066]

3. Results

The results are also shown in Tables 1 and 2.

Experimental Examples 1 to 10 and 13 to 20 satisfy the following requirements (a) to (c). In contrast, Experimental Examples 11 and 12 do not satisfy the requirement (b). In

Experimental Examples 1 to 10 and 13 to 20, the compressive stress 50% was lower than Experimental Examples 11 and 12, and the number of cells was larger than Experimental Examples 11 and 12. In Experimental Examples 1 to 10 and 13 to 18, the "density", the "compressive stress 50%", the "compression set", and the "gel fraction" showed good physical property values.

- Requirement (a): the resin composition contains a polyolefin-based resin containing at least an ethylene-vinyl acetate copolymer.

- Requirement (b): the resin composition contains a petroleum resin and/or a styrene-based resin.

- Requirement (c): the resin composition is foamed.

[0067]

Experimental Examples 1, 2, 9, 10, 14, 15, and 16 among Experimental Examples 1 to 10 satisfy the following requirement (d). In contrast, Experimental Examples 11 and 12 do not satisfy the requirement (d). In Experimental Examples 1, 2, 9, 10, 14, 15 and 16, the evaluation of the water sealing property was "pass", and the resin foams were excellent in water sealing property.

- Requirement (d): the resin composition contains a silicone resin.

[0068]

4. Effects of Examples

According to the above Examples, it is possible to provide a resin foam having a good foam-breaking property and

fine cells.

[0069]

The present disclosure is not limited to the embodiment described in detail above, and various modifications or changes can be made.

CLAIMS

1. A resin foam obtained by foaming a resin composition containing: a polyolefin-based resin containing at least an ethylene-vinyl acetate copolymer; and a petroleum resin and/or a styrene-based resin.
2. The resin foam according to claim 1, wherein the petroleum resin and/or the styrene-based resin is contained in an amount of 2.0 parts by mass or more and 20 parts by mass or less based on 100 parts by mass of the total of the polyolefin-based resin.
3. The resin foam according to claim 1 or 2, wherein the resin composition contains a silicone resin.
4. The resin foam according to claim 3, wherein the silicone resin is contained in an amount of more than 0 parts by mass and 10 parts by mass or less based on 100 parts by mass of the total of the polyolefin-based resin.
5. The resin foam according to any one of claims 1 to 4, wherein the number of cells based on JIS K6767 is 50 cells/25 mm or more.