EUROPEAN PATENT SPECIFICATION

(54) Expandable rubber-modified styrene resin composition
     Dehnbare Gummimodifizierte Styrene Harzzusammensetzung
     Composition expansible de résine styrénique modifiée par un caoutchouc

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     US-A- 5 525 637
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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an expandable rubber-modified styrene resin composition to obtain a molded foam having an excellent impact resistance and pliability as well as a high expansion ratio and also relates to a molded foam obtained by said expandable rubber-modified styrene resin composition.

Description of the Related Art

[0002] A molded foam made from a polystyrene resin is employed widely as a container and a heat insulating material for its excellent shock-absorbing properties and heat-insulating properties as well as easiness in molding into an article. However, because of its insufficient impact resistance and pliability which may cause formation of cracks and breaks, it involves problems such as difficulty in applying to a package for a precision instrument.

[0003] On the other hand, a molded foam made from a polypropylene resin requires a large-scaled device for molding although it has excellent impact resistance and pliability. Further, its resin characteristics also requires a transportation from a manufacturer to a molding company in a form of pre-expanded beads. As a result, a production cost becomes disadvantageously high.

[0004] Recently, a rubber-modified styrene resin molded foam which is easy to be molded and has improved impact resistance and pliability compared with a polystyrene foam has been proposed in Japanese Laid-Open Patent Publication Nos.3-182529, 5-116227, 7-11043 and 7-90105.

[0005] US 5 525 637 discloses an expandable styrene polymer for elastic polystyrene foams comprising polystyrene and/or or a styrene copolymer, at least one styrene soluble elastomer comprising a polybutadiene rubber, at least one block copolymer containing styrene and a polymerizable ethylenically unsaturated monomer as one component, a low boiling blowing agent and, if desired, conventional additives. Furthermore, this document discloses an elastic foam prepared from said expandable styrene polymer.

[0006] Nevertheless, the impact resistance and the pliability of a conventional molded foam is improved only to a limited and insufficient degree, and attempts to achieve a high expansion ratio result in obtaining a molded foam having a poor appearance due to shrinkage and a reduced strength. Accordingly, it is impossible to use a molded foam as being foamed at a high expansion ratio, resulting in a limitation in package resource saving.

SUMMARY OF THE INVENTION

[0007] Therefore, an object of the present invention is to provide an expandable rubber-modified styrene resin composition that is enabled to obtain a molded foam having a high expansion ratio, excellent impact resistance and pliability and satisfactory appearance.

[0008] The present invention is an expandable rubber-modified styrene resin composition comprising 85 to 99 % by weight of a rubber-modified styrene resin containing a rubber particle of a diene polymer dispersed in a continuous phase of a styrene resin and 1 to 15 % by weight of a volatile blowing agent whose boiling point is 80°C or lower, wherein:

- the weight-average molecular weight of said continuous phase of the styrene resin is 150,000 to 300,000;
- the graft ratio of the styrene resin to the diene polymer is 70 to 135 %; and,
- the swelling index of the gel fraction of said diene polymer in toluene at 25°C is 12 to 25.

[0009] According to the present invention, an expandable rubber-modified styrene resin composition that is enabled to obtain a molded foam having a high expansion ratio, excellent impact resistance and pliability and satisfactory appearance can be provided.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The styrene resin described above can for example be produced by dissolving a diene polymer in an aromatic vinyl compound such as styrene, p-methylstyrene and α-methylstyrene followed by effecting radical polymerization in the presence of an azo compound such as azobisisobutyronitrile or a peroxide such as benzoyl peroxide and t-butylperoxybenzoate with employing bulk polymerization, solution polymerization, suspension polymerization, bulk-suspension polymerization or the like.

[0011] The weight-average molecular weight of the styrene resin described above is 150,000 to 300,000. When the
weight-average molecular weight is less than 150,000, strength of a molded foam may become lower, while that exceeding 300,000 causes difficulty in producing a molded foam. The weight-average molecular weight is preferably 180,000 to 250,000.

[0012] The diene polymer described above can be a polymer of a diene compound such as butadiene and isoprene or a copolymer with an aromatic vinyl compound such as styrene capable of being copolymerized with a diene compound. Preferably, a butadiene polymer is employed.

[0013] Preferably, the rubber-modified styrene resin described above preferably contains 5 to 20 % by weight of a diene polymer.

[0014] A content less than 5 % by weight may cause difficulty in obtaining a molded foam having satisfactory impact resistance and pliability. On the other hand, a content exceeding 20 % by weight may not provide an increase in strength corresponding to an increase in the amount and results in adverse effects on moldability such as melting of the surface of the molded foam.

[0015] More preferably, the content is in a range of 7 to 15 % by weight.

[0016] The graft ratio of a styrene resin to a diene polymer is in a range of 70 to 135 %. A graft ratio less than 70 % may not provide a molded foam having sufficient impact resistance and pliability. On the other hand, a graft ratio exceeding 135 % may not cause much orientation of the rubber particle in a foam membrane, resulting in difficulty in foaming, which may lead to shrinkage or deformation in a molded foam of a high expansion ratio. Preferably, the graft ratio is 80 to 130 %. More preferably, the ratio is 100 to 120 %.

[0017] The graft ratio described above is a value defined as follows.

\[
\text{[Graft ratio]} = \frac{[\text{Gel fraction-Diene polymer content}] \times 100}{[\text{Diene polymer content}]}
\]

[0018] The content described above is the weight (%) based on the rubber-modified styrene resin.

[0019] The swelling index of the gel fraction of the diene polymer in toluene at 25°C is 12 to 25. A swelling index of the gel fraction less than 12 may not cause much orientation of the rubber particle in a foam membrane, resulting in difficulty in foaming, which may lead to shrinkage or deformation in a molded foam of a high expansion ratio. On the other hand, a swelling index exceeding 25 does not allow a molded foam having sufficient impact resistance and pliability. Preferably, the swelling index is 13 to 20. More preferably, the swelling index is 15 to 20.

[0020] The swelling index of the gel fraction of a diene polymer is a value defined as follows.

\[
\text{[Swelling index]} = \frac{[\text{Weight of gel swollen in toluene at 25°C}]}{[\text{Dry gel weight}]}
\]

[0021] In an expandable rubber-modified styrene resin composition, 85 to 99 % by weight of a rubber-modified styrene resin described above is contained.

[0022] A volatile blowing agent having a boiling point of 80°C or lower is employed.

[0023] In an expandable rubber-modified styrene resin composition, the volatile blowing agent described above is contained in an amount of 1 to 15 % by weight. A content less than 1 % by weight results in an insufficient foaming capability, and accordingly a predetermined expansion ratio can not be achieved. On the other hand, a content exceeding 15 % by weight involves a problem that shrinkage and deformation may occur when producing a molded foam.

[0024] The volatile blowing agent described above can be an organic compound having a boiling point of 80°C or lower such as propane, butane, isobutane, pentane, isopentane, neopentane, cyclopentane, hexane, trichlorofluoromethane, dichlorofluoromethane, dichlorotetrafluoroethane, chloromethane, dichloromethane, methanol, diethylether and the like, which may be used singly or in combination.

[0025] Preferably, the expandable rubber-modified styrene resin composition described above contains a plasticizer for the purpose of imparting the molded foam with pliability.

[0026] Such a plasticizer can be esters such as dioctyl phthalate and dioctyl adipate, hydrocarbons such as toluene, xylene and cyclohexane, fatty esters of polyhydric alcohols such as glycerin tristearate and glycerin trioctoate as well as mineral oils, liquid paraffin and the like.

[0027] The expandable rubber-modified styrene resin composition described above may also contain one or more additives such as inorganic fillers, lubricants, flame retardants, antioxidants, antistatic agents, UV absorbers and carbon black.

[0028] Thus, an expandable rubber-modified styrene resin composition may contain inorganic fillers such as talc,
clay, calcium carbonate and titanium oxide, lubricants such as aluminum stearate, zinc stearate, aluminum p-t-butylbenzoate and ethylene bis-stearyl amide, flame retardants such as tris(dibromomethyl) phosphate, pentabromodiphenyl ether, tetrabromobutane, dibromomethylbenzol and 1,2,5,6,9,10-hexabromocyclodecane, as well as antioxidants, antistatic agents, UV absorbers and carbon black and the like.

[0029] The particle size of the diene polymer rubber particle dispersed in the continuous phase of a styrene polymer is preferably 2 to 10 µm.

[0030] A particle size less than 2 µm may cause difficulty in obtaining a molded foam having sufficient impact resistance and pliability. On the other hand, a particle size exceeding 10 µm may result in too large a rubber particle to effect appropriate expanding, which may lead to shrinkage and deformation when producing a molded foam. More preferably, the particle size is 3 to 7 µm.

[0031] Preferably, a diene polymer comprises a 1,4-cis structure at a ratio of 80 % or more.

[0032] A ratio of the 1,4-cis structure less than 80 % may yield a molded foam having insufficient pliability and impact resistance when an inventive expandable composition is employed. More preferably, the ratio is 90 % or more, or the entire of the polymer is in the 1,4-cis structure.

[0033] The expandable rubber-modified styrene resin composition described above can be produced by, for example, kneading and fusing a rubber-modified styrene resin and a volatile blowing agent in an extruder, extruding via a pore of the die on the tip of the extruder, introducing into water for rapid cooling, pelletizing still in the state of a non-expanded material, thereby producing an expandable rubber-modified styrene resin composition.

[0034] Alternatively, a rubber-modified styrene resin can be kneaded and fused in an extruder and extruded via a pore of the die on the tip of the extruder, and pelletized by strand cut, hot cut, under water cut and the like into a particle having a size of 0.5 to 5 mg/piece, and the particle of the rubber-modified styrene resin thus obtained is placed in an autoclave and dispersed in an aqueous medium in the presence of a suspending agent, and the resin particle is impregnated with a volatile blowing agent, whereby producing an expandable rubber-modified styrene resin composition.

[0035] An expandable rubber-modified styrene resin composition according to the present invention is pre-expanded by heating to obtain a pre-expanded bead of a rubber-modified styrene resin.

[0036] In the obtained pre-expanded beads, the rubber particles are flatly dispersed in the surface direction of a foam membrane of the pre-expanded beads. When the foam membrane is observed in section in the thickness direction, the relation between the rubber particles, which lamelarly present in plural, is characterized in that the average amount of the aspect ratio (b/a) of a size of the rubber particle in the surface direction of the foam membrane (b) to a size of the rubber particle in the thickness direction of the foam membrane (a) is 60 or more. The average value is preferably more than 70, and further preferably more than 80. When this value is less than 60, the physical properties, such as resistance to cracking, are lowered, and thus sufficient impact resistance and pliability may not be obtained. The pre-expanding can be effected by, for example, heating to a temperature close to a glass transition temperature of the pre-expanded bead, or fusing the pre-expanded bead with another, and after cooling for a certain period the molded foam is released from the mold. The density of the molded foam article in this case is usually in a range of 14 to 50 kg/m³ and preferably 16 to 20 kg/m³. When the density of the molded foam article exceeds 50 kg/m³, the production cost may be increased. When the density of the molded foam article is less than 14 kg/m³, the strength may be weakened. The molded foam article thus obtained having a high quality with an excellent impact resistance, wherein the 50 % failure height in a fallen ball impact test is more than 40 cm at 50 - 55 x expanding magnification, and moreover, this article can be easily obtained.

[0037] The pre-expanded bead of a rubber-modified styrene resin can also be molded using a molding machine employed for production of a polystyrene molded foam. Namely, the pre-expanded bead is packed in a mold, which is then heated by a steam to post-expand the pre-expanded bead and fuse the pre-expanded bead to each other, and after cooling for a certain period the molded foam is released from the mold. The density of the molded foam article in this case is usually in a range of 14 to 50 kg/m³ and preferably 16 to 20 kg/m³. When the density of the molded foam article exceeds 50 kg/m³, the production cost may be increased. When the density of the molded foam article is less than 14 kg/m³, the strength may be weakened. The molded foam article thus obtained having a high quality with an excellent impact resistance, wherein the 50 % failure height in a fallen ball impact test is more than 40 cm at 50 - 55 x expanding magnification, and moreover, this article can be easily obtained.

Embodiments

[0038] An expandable rubber-modified styrene resin composition and a method for producing the same according to the embodiment of the present invention are described below sequentially with referring to typical examples.

Examples 1 to 5 and Comparative Examples 1 and 2

(1) Method for Producing Rubber-Modified Styrene Resin

[0039] A rubber-modified styrene resin was produced by bulk polymerization.

[0040] Thus, 100 parts by weight of a styrene monomer was intermixed and dissolved with 10 parts by weight of butadiene polymer, 0.03 parts by weight of t-butyl peroxybenzoate and 12 parts by weight of ethylbenzene. The mixture was continuously pumped into a 30 L reactor fitted with a stirrer at the average residence time of 2.5 hours, whereby effecting the polymerization of the styrene monomer at a temperature of 110 to 130°C.
Subsequently, the reaction mixture thus obtained was pumped continuously to two groups of PLUGFLOW-type reactors, in which polymerization reaction was conducted at temperatures of 120 to 130°C and 150 to 180°C, respectively, until final polymer conversion became 80 to 90%. Thereafter, unreacted styrene monomer and the solvent were removed by evaporation under a reduced pressure with heating, and the mixture was pelletized to obtain an intended rubber-modified styrene resin.

Based on the polymerization procedure described above but varying the temperature of the reactor and the evaporation tank, rubber-modified styrene resins having different graft ratios, different gel swelling index and different rubber particle sizes were obtained. Also by varying the concentration of the butadiene polymer to be supplied to the styrene monomer described above, the butadiene polymer content in the rubber-modified styrene resin was adjusted.

(2) Method for Producing Expandable Rubber-Modified Styrene Resin Composition

Each of the rubber-modified styrene resins obtained as described above (Table 1) was fluxed by means of a 65 mm single extruder, cut under water to obtain a resin particle having a size of about 1.3 mg/piece. Subsequently, a 3 L autoclave fitted with a stirrer was charged with 100 parts by weight of each resin particle described above, 150 parts by weight of deionized water, 0.7 parts by weight of sodium pyrophosphate, 1.4 parts by weight of magnesium sulfate, 3 parts by weight of sodium sulfate and 0.075 parts by weight of sodium lauryl sulfate, and the reactor was then closed tightly.

After heating the autoclave to 100°C with stirring, a volatile blowing agent consisting of 4 parts by weight of pentane and 8 parts by weight of butane was pressed into the autoclave, which was then kept at 100°C for 5 hours. After cooling to 30°C, the resin particle impregnated with the blowing agent was recovered and washed with water and dehydrated.

Then the resin particle was put into a cylindrical metal container fitted with 0.1 mm mesh size sieves provided with the each end of the metal container, and dried nitrogen at room temperature was introduced from the bottom of the cylindrical metal container at the flow rate of 500 L per minute over a period of 10 minutes to dry the particle. As a result, an expandable rubber-modified styrene resin composition was obtained.

(3) Production of Pre-Expanded Bead and Molded Foam

100 Parts by weight of the resin particle of an expandable rubber-modified styrene resin composition obtained as described above was coated with a mixture of 0.04 parts by weight of an antistatic agent and 0.06 parts by weight of an anti-lumping agent, and then allowed to stand at 0°C for 24 hours.

Then pre-expansion by about 55 times was conducted by introducing a steam at 0.1 MPa using a stirrer-fitted batch pre-expander for an expandable polystyrene and then a pre-expanded bead of the rubber-modified styrene resin was obtained.

After allowing the obtained pre-expanded bead to stand at room temperature for one day, a molded foam of the rubber-modified styrene resin was produced using a molding machine for polystyrene foaming molding (Model VS-500; manufactured by Daisen Industry Co., Ltd.).

(4) Evaluation of Expandable Rubber-Modified Styrene Resin Compositions

1) Weight-Average Molecular Weight of Styrene Resin Continuous Phase

A rubber-modified styrene resin was dissolved in THF (tetrahydrofuran) and the insolubles were filtered off with a membrane filter, and then the weight-average molecular weight was determined by gel permeation chromatography (GPC).

2) Swelling Index of Gel fraction of Diene Polymer

About 1 g of an expandable rubber-modified styrene resin composition was admixed with 30 ml of methyl-ethylketone, allowed to be dipped at 25°C for 24 hours, shaken for 5 hours, and then centrifuged at 5°C and 18,000 rpm for 1 hour.

After decanting the supernatant off, 30 ml of toluene was newly added and the mixture was subjected to shaking at 25°C for 1 hour followed by centrifugation at 5°C and 18,000 rpm for 2 hours. After removing the supernatant, the centrifugal pellet was weighed (weight of gel swollen in toluene at 25°C).

After drying in vacuum at 60°C for 8 hours, the residue was weighed (dry gel weight). The gel swelling index was determined according to the formula shown below.
3) Graft Ratio

The graft ratio was calculated according to the formula shown below.

\[
\text{Graft ratio} = \frac{\% \text{ Gel by weight} - \% \text{ Diene polymer by weight}}{\% \text{ Diene polymer by weight}} 
\times 100
\]

4) Particle Size of Diene Polymer Rubber Particle

The particle size of a diene polymer rubber particle was determined by analysis of the rubber particle dispersed in DMF (dimethylformamide) as a solvent using a laser diffraction/scattering particle size distribution analyzer model LA-700 manufactured by HORIBA SEISAKUSHO Co., Ltd. followed by calculation from the volume-based particle size distribution obtained according to the formula shown below.

\[
\text{Particle size} = \frac{\sum D_i^4 \times N_i}{\sum D_i^3 \times N_i}
\]

5) Volatile Blowing Agent Content

A weighed sample, i.e., an expandable rubber-modified styrene resin composition was heated at 120°C for 4 hours, weighed to obtain the difference between the weight before heating and that after heating which was used to calculate the total volatile content (% by weight) from which the water content (% by weight) determined by Karl Fischer method was subtracted to give the volatile blowing agent content. Volatile blowing agent content (% by weight) = [Sample weight after heating (g) x 100 / Sample weight before heating (g)] - water content (% by weight)

6) Molded foam density

From the weight of a molded foam (kg) and the volume of the molded foam (m³) based on a mold size, the molded foam density (kg/m³) was obtained.

7) Surface Appearance

The appearance of the surface of a molded foam was evaluated according to the criteria shown below.

○: Almost no shrinkage, burned surface or voids were observed.
△: Shrinkage, burned surface or voids were observed.
×: Marked shrinkage, burned surface or voids were observed.

8) 50 % Failure Height

A molded foam was cut into test pieces each being 200 mm in length, 40 mm in width and 25 mm in thickness, onto which a 255 g steel ball was fallen down to determine the 50 % failure height (cm) in accordance with JIS K 7211 (Japanese Industrial Standard). Based on the height thus obtained, the impact resistance was evaluated.
9) Pliability

[0061] A molded foam was cut into test pieces each being 200 mm in length, 30 mm in width and 20 mm in thickness. 10 metal cylinders having diameters ranging from 100 to 10 mm were provided and the center of each test piece was pressed against a cylinder and wound around the cylinder at a constant speed for about 5 seconds.

[0062] The test was started with the cylinder having the diameter of 100 mm, and when the test piece was not broken then the cylinder having the diameter which was shorter by 10 mm than that of the previous cylinder was used to conduct the test similarly. Until the piece was broken, the test was continued successively with a series of the cylinder having the diameter which was shorter by 10 mm than that of the previous cylinder. Once the test piece was broken, the diameter of the previous cylinder was recorded. Pliability was judged based on the mean value (mm) of 10 test pieces. Thus a lower value represented a higher pliability.

(10) Aspect Ratio (b/a)

[0063] An aspect ratio (b/a) is defined as a ratio of a size of the rubber particle in the surface direction of the foam membrane (b) to a size of the rubber particle in the thickness direction of the foam membrane (a). The rubber particles are flatly dispersed in the surface direction of the foam membrane of the pre-expanded beads and laminarily present in plural when the foam membrane is observed in a section in the thickness direction. The aspect ratio (b/a) was measured by the following process.

[0064] Initially, part of the pre-expanded bead was cut out and then embedded in a low-viscosity epoxy resin. Then, the obtained was dipped in an osmium oxide (OsO₄) solution followed by preparation of an ultra-thin pellicle slice using a microtome. The values (a) and (b) was measured by transmission electron microscope observation. The aspect ratio (b/a) was determined as an average value of the aspect ratio of 25 of the rubber particles randomly selected.

[0065] The results of Examples and Comparatives are shown in Table 1.

[0066] The results shown in Table 1 indicated the characteristics described below.

[0067] Thus, the molded foams of Examples 1 to 5 according to the present invention exhibited excellent appearance of the surface of the molded foams, higher impact resistance (50 % failure height) and satisfactory pliability, even at a high expansion ratio (x 55, density: about 18 kg/m³).

[0068] On the other hand, when a rubber-modified styrene resin having a higher graft ratio and a lower swelling index (Comparative Examples 1 and 2) was employed, the impact resistance and the pliability were poor at a high expansion ratio.
| Examples | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| Weight-average molecule weight (x 10^4) | 26 | 26 | 22 | 23 | 22 | 22 | 20 | 20 | 17 | 17 | 16 | 16 | 15 | 15 | 14 | 14 | 13 | 13 | 12 | 12 |
| Swelling index | 90 | 90 | 80 | 80 | 100 | 100 | 133 | 133 | 140 | 140 | 12 | 12 | 10 | 10 | 11 | 11 | 12 | 12 | 11 | 11 |
| Rubber particle size (µm) | 5 | 5 | 4 | 4 | 5 | 5 | 1 | 1 | 5 | 5 | 3 | 3 | 3 | 3 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Ratio of cis structure (wt %) | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 |
| Volatilize foaming agent content (%) | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O | O |
| Molded foam density (kg/m³) | 6.7 | 6.7 | 6.5 | 6.5 | 7.0 | 7.0 | 8.0 | 8.0 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 | 8.6 |
| Surface appearance (O/ΔX) | 10.0 | 10.0 | 18.5 | 18.5 | 18.1 | 18.1 | 17.9 | 17.9 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 |
| 50% failure height (cm) | 52 | 52 | 48 | 48 | 46 | 46 | 43 | 43 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 |
| Pliability (mm) | 52 | 52 | 61 | 61 | 50 | 50 | 65 | 65 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 |
| Aspect ratio (b/a) | 120 | 120 | 107 | 107 | 136 | 136 | 90 | 90 | 76 | 76 | 76 | 76 | 76 | 76 | 76 | 76 | 76 | 76 | 76 | 76 |
Claims

1. An expandable rubber-modified styrene resin composition comprising 85 to 99 % by weight of a rubber-modified styrene resin containing a rubber particle of a diene polymer dispersed in a continuous phase of a styrene resin and 1 to 15 % by weight of a volatile blowing agent whose boiling point is 80°C or lower, wherein:

- the weight-average molecular weight of said continuous phase of the styrene is 150,000 to 300,000;
- the graft ratio of the styrene resin to the diene polymer is 70 to 135 %; and,
- the swelling index of the gel fraction of said diene polymer in toluene at 25°C is 12 to 25.

2. An expandable rubber-modified styrene resin composition according to claim 1, wherein said rubber particle of the diene polymer dispersed in the continuous phase of the styrene resin is 2 to 10 μm.

3. An expandable rubber-modified styrene resin composition according to claim 1 or 2, wherein said diene polymer comprises a 1,4-cis structure at a ratio of 80 % or more.

4. An expandable rubber-modified styrene resin composition according to any one of claims 1 to 3, wherein said diene polymer is a polymer of butadiene or isoprene.

5. An expandable rubber-modified styrene resin composition according to any one of claims 1 to 4, wherein said rubber-modified styrene resin contains 5 to 20 % by weight of a diene polymer.

6. An expandable rubber-modified styrene resin composition according to any one of claims 1 to 5, wherein the expandable rubber-modified styrene resin composition contains a plasticizer for the purpose of imparting pliability thereto.

7. A molded foam comprising a rubber-modified styrene resin composition comprising a rubber particle of a diene polymer dispersed in a continuous phase of a styrene resin, wherein:

- the weight-average molecular weight of said continuous phase of the styrene is 150,000 to 300,000;
- the graft ratio of the styrene resin to the diene polymer is 70 to 135 %;
- the swelling index of the gel fraction of said diene polymer in toluene at 25°C is 12 to 25; and
- the density of the form is in a range of 14 to 50 kg/m³.

8. A molded foam according to claim 7, wherein a 50 % failure height at a falling ball impact test is 40 cm or more when the molded foam article comprises a density of 16 to 20 kg/m³.

9. A molded foam according to claim 7 or 8, wherein said rubber particles in the pre-expanded bead forming the molded foam are flatly dispersed in the surface direction of a foam membrane of the pre-expanded bead and laminarly present in plural when the foam membrane is observed in a section in the thickness direction, wherein an average amount of an aspect ratio (b/a) of a size of the rubber particle in the surface direction of the foam membrane (b) to a size of the rubber particle in the thickness direction of the foam membrane (a), is 60 or more.

10. A molded foam according to any one of claims 7 to 9, wherein said rubber particle of the diene polymer dispersed in the continuous phase of the styrene resin is 2 to 10 μm.

11. A molded foam according to any one of claims 7 to 10, wherein said diene polymer comprises a 1,4-cis structure at a ratio of 80 % or more.

12. A molded foam according to any one of claims 7 to 11, wherein said diene polymer is a polymer of butadiene or isoprene.

13. A molded foam according to any one of claims 7 to 12, wherein said rubber-modified styrene resin contains 5 to 20 % by weight of a diene polymer.

14. A molded foam according to any one of claims 7 to 13, wherein the expandable rubber-modified styrene resin composition contains a plasticizer for the purpose of imparting pliability thereto.
Patentansprüche

1. Eine schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung, die 85 bis 99 Gew.-% eines Kautschuk-
modifizierten Styrolharzes, das Kautschukteilchen aus einem Dienpolymer enthält, die in einer kontinuierlichen
Phase eines Styrolharzes dispergiert sind, und 1 bis 15 Gew.-% eines flüchtigen Treibmittels umfasst, dessen
Siedepunkt bei 80°C oder weniger liegt, wobei
das Gewichtsmittel des Molekulargewichts der kontinuierlichen Phase des Styrolharzes 150000 bis 300000
beträgt,
das Pfropfverhältnis des Styrolharzes zu dem Dienpolymer 70 bis 135 % beträgt und

2. Schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung nach Anspruch 1, bei der die Kautschukteil-
chen aus dem Dienpolymer, die in der kontinuierlichen Phase des Styrolharzes dispergiert sind, 2 bis 10 µm groß
sind.

3. Schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung nach Anspruch 1 oder 2, bei der das Dienpo-
lymer eine 1,4-cis-Struktur in einem Anteil von 80 % oder mehr umfasst.

4. Schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung nach einem der Ansprüche 1 bis 3, bei der das
Dienpolymer ein Polymer aus Butadien oder Isopren ist.

5. Schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung nach einem der Ansprüche 1 bis 4, bei der das
Kautschuk-modifizierte Styrolharz 5 bis 20 Gew.-% eines Dienpolymers enthält.

6. Schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung nach einem der Ansprüche 1 bis 5, bei der die
schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung einen Weichmacher enthält, um der Zusam-
mensetzung eine Biegsamkeit zu verleihen.

7. Ein geformter Schaum, der eine Kautschuk-modifizierte Styrolharzzusammensetzung umfasst, die Kautschukteil-
chen aus einem Dienpolymer umfasst, die in einer kontinuierlichen Phase eines Styrolharzes dispergiert sind,
wobei
das Gewichtsmittel des Molekulargewichts der kontinuierlichen Phase des Styrolharzes 150000 bis 300000
beträgt,
das Pfropfverhältnis des Styrolharzes zu dem Dienpolymer 70 bis 135 % beträgt,
der Quellungsindex der Gelfraktion des Dienpolymers in Toluol bei 25°C 12 bis 25 beträgt, und
die Dichte des Schaums in einem Bereich von 14 bis 50 kg/m³ liegt.

8. Geformter Schaum nach Anspruch 7, bei dem die 50 % Bruchfallhöhe bei einem Kugelfall-Schlagtest 40 cm oder
mehr beträgt, wenn der geformte Schaumgegenstand eine Dichte von 16 bis 20 kg/m³ umfasst.

9. Geformter Schaum nach Anspruch 7 oder 8, bei dem die Kautschukteilchen in den vorgeschäumten Kügelchen,
die den geformten Schaum bilden, flach in der Oberflächenrichtung einer Schaummembran des vorgeschäumten
Kügelchens dispergiert sind und in einer Mehrzahl laminar vorliegen, wenn die Schaummembran in einem Schnitt
in der Dickenrichtung betrachtet wird, wobei der durchschnittliche Betrag des Seitenverhältnisses (b/a) der Größe
der Kautschukteilchen in der Oberflächenrichtung der Schaummembran (b) zu der Größe der Kautschukteilchen
in der Dickenrichtung der Schaummembran (a) 60 oder mehr beträgt.

10. Geformter Schaum nach einem der Ansprüche 7 bis 9, bei dem die Kautschukteilchen aus dem Dienpolymer, die
in einer kontinuierlichen Phase des Styrolharzes dispergiert sind, 2 bis 10 µm groß sind.

11. Geformter Schaum nach einem der Ansprüche 7 bis 10, bei dem das Dienpolymer eine 1,4-cis-Struktur in einem
Anteil von 80 % oder mehr umfasst.

12. Geformter Schaum nach einem der Ansprüche 7 bis 11, bei dem das Dienpolymer ein Polymer aus Butadien oder
Isopren ist.

13. Geformter Schaum nach einem der Ansprüche 7 bis 12, bei dem das Kautschuk-modifizierte Styrolharz 5 bis 20
Gew.-% eines Dienpolymers enthält.
14. Geformter Schaum nach einem der Ansprüche 7 bis 13, bei dem die schäumbare Kautschuk-modifizierte Styrolharzzusammensetzung einen Weichmacher enthält, um der Zusammensetzung eine Biegsamkeit zu verleihen.

**Revendications**

1. Composition expansible de résine styrénique modifiée base caoutchouc comprenant de 85 à 99 % en poids d'une résine styrénique modifiée par du caoutchouc contenant une particule de caoutchouc d'un polymère diényque dispersé dans une phase continue d'une résine styrénique et de 1 à 15 % en poids d'un agent porogène volatil, dont le point d'ébullition est de 80°C ou est inférieur à 80°C, dans laquelle :

   - la masse moléculaire moyenne en poids de la phase continue du styrène est comprise entre 150 000 et 300 000 ;
   - le rapport de greffage de la résine styrénique au polymère diényque est compris entre 70 et 135 % ; et
   - l'indice de gonflement de la fraction de gel du polymère diényque dans le toluène à 25°C est compris entre 12 et 25.

2. Composition expansible de résine styrénique modifiée par caoutchouc suivant la revendication 1, dans laquelle la particule de caoutchouc du polymère diényque dispersé dans la phase continue de la résine styrénique est comprise entre 2 et 10 µm.

3. Composition expansible suivant la revendication 1 ou 2, dans laquelle le polymère diényque comprend une structure 1,4-cis en un rapport de 80 % ou supérieur à 80 %.

4. Composition expansible suivant l'une quelconque des revendications 1 à 3, dans laquelle le polymère diényque est un polymère de butadiène ou d'isoprène.

5. Composition expansible suivant l'une quelconque des revendications 1 à 4, dans laquelle la résine styrénique modifiée par du caoutchouc contient de 5 à 20 % en poids d'un polymère diényque.

6. Composition expansible suivant l'une quelconque des revendications 1 à 5, dans laquelle la composition expansible de résine styrénique modifiée par du caoutchouc contient un plastifiant pour lui donner de l'aptitude à se plier.

7. Mousse moulée comprenant une composition de résine styrénique modifiée par du caoutchouc comprenant une particule de caoutchouc d'un polymère diényque dispersé dans une phase continue d'une résine styrénique, dans laquelle :

   - la masse moléculaire moyenne en poids de la phase continue du styrène est comprise entre 150 000 et 300 000 ;
   - le rapport de greffage de la résine styrénique au polymère diényque est compris entre 70 et 135 % ; et
   - l'indice de gonflement de la fraction de gel du polymère diényque dans le toluène à 25°C est compris entre 12 et 25 ; et
   - la masse volumique de la mousse est comprise entre 14 et 50 kg/m³.

8. Mousse moulée suivant la revendication 7, dans laquelle la hauteur de défaillance à 50 % dans un essai de choc par chute d'une bille est de 40 cm ou est supérieure à 40 cm, lorsque l'objet en mousse moulée a une masse volumique de 16 à 20 kg/m³.

9. Mousse moulée suivant la revendication 7 ou 8, dans laquelle les particules de caoutchouc dans la perle pré-expansée formant la mousse moulée sont dispersées à plat dans la direction de la surface d'une membrane de mousse de la perle pré-expansée et se présente laminairement en pluralité lorsque l'on observe la membrane mousse suivant une coupe dans la direction de l'épaisseur, une valeur moyenne d'un rapport d'aspect (b/a), une dimension de la particule de caoutchouc dans la direction de la surface de la membrane de mousse (b) à une dimension de la particule du caoutchouc dans la direction de l'épaisseur de la membrane de mousse (a), étant de 60 ou supérieure à 60.

10. Mousse moulée suivant l'une quelconque des revendications 7 à 9, dans laquelle la particule de caoutchouc du polymère diényque dispersé dans la phase continue de la résine styrénique est comprise entre 2 et 10 µm.
11. Mousse moulée suivant l'une quelconque des revendications 7 à 10, dans laquelle le polymère diénique comprend une structure 1,4-cis en un rapport de 80 % ou supérieur à 80 %.

12. Mousse moulée suivant l'une quelconque des revendications 7 à 11, dans laquelle le polymère diénique est un polymère de butadiène ou d'isoprène.

13. Mousse moulée suivant l'une quelconque des revendications 6 à 12, dans laquelle la résine styrénique modifiée par du caoutchouc contient 5 à 20 % en poids d'un polymère diénique.

14. Mousse moulée suivant l'une quelconque des revendications 7 à 13, dans laquelle la composition expansible de résine styrénique modifiée par du caoutchouc contient un plastifiant afin de lui donner de l'aptitude à se plier.