

[Name of the Document] Specification

[Title of the Invention] STYRENE-MODIFIED LINEAR
LOW-DENSITY POLYETHYLENE-BASED RESIN BEADS,
STYRENE-MODIFIED LINEAR LOW-DENSITY

5 POLYETHYLENE-BASED EXPANDABLE RESIN BEADS,
PRODUCTION METHOD THEREFOR, PRE-EXPANDED BEADS
AND EXPANDED MOLDED ARTICLE

[Technical Field]

10 The present invention relates to styrene-modified
linear low-density polyethylene-based resin beads,
styrene-modified linear low-density polyethylene-based
expandable resin beads, production method therefor,
pre-expanded beads and an expanded molded article.

15

[Background Art]

A polyethylene-based resin foam is generally used as a
packing material owing to its high elasticity and excellent oil
and impact resistance. The polyethylene-based resin foam,
20 however, has weakness that its stiffness and compressive
strength are low. On the other hand, a styrene-based resin
foam is excellent in stiffness, but has a weakness that it is
brittle.

To overcome such weakness, Japanese Examined
25 Patent Publication No. SHO 51(1976)-46138 (Patent Document

1), Japanese Examined Patent Publication No. SHO
52(1977)-10150 (Patent Document 2), Japanese Examined
Patent Publication No. SHO 58(1983)-53003 (Patent Document
3) and Japanese Unexamined Patent Publication No. SHO
5 62(1987)-59642 (Patent Document 4) disclose methods in
which polyethylene-based resin is impregnated with a
styrene-based monomer and polymerization is performed to
obtain styrene-modified polyethylene-based expandable resin
beads. The polyethylene-based resins used in these methods
10 are mostly low-density polyethylene, high-density polyethylene,
and ethylene/vinyl acetate copolymer. Since the
styrene-based monomer cannot be sufficiently dispersed in
such polyethylene-based resins, the polyethylene-based resin
needs to be crosslinked in order to provide sufficient stiffness
15 and impact resistance.

Japanese Patent No. 2668384 (Patent Document 5)
discloses a method for obtaining an expanded molded article of
modified polyethylene-based resin excellent in stiffness and
impact resistance. In this method, 100 parts by weight of
20 non-crosslinked linear low-density polyethylene-based resin
beads, 5 to 300 parts by weight of a vinyl aromatic monomer,
and 1 to 3 parts by weight of a polymerization initiator relative
to 100 parts by weight of the vinyl aromatic monomer are
dispersed in an aqueous medium. Then, the resulting
25 suspension is heated to such a temperature that the monomer

does not substantially polymerize to impregnate the inside and the surface of the polyethylene-based resin beads with the monomer. Subsequently, the temperature of the suspension is raised to polymerize the monomer and a vinyl aromatic
5 polymer is micro-dispersed in the polyethylene-based resin to obtain the expanded molded article of modified polyethylene-based resin.

In the above patent, there is no disclosure on linear low-density polyethylene obtained by using a metallocene
10 compound as a catalyst. The non-crosslinked linear low-density polyethylene-based resin beads (ULT-ZEX 3021F manufactured by Mitsui Chemicals, Inc.) described in its Examples are linear low-density polyethylene obtained by polymerization using an ordinary Ziegler-Natta catalyst.

15 [Patent Document 1] Japanese Examined Patent Publication No. SHO 51(1976)-46138

[Patent Document 2] Japanese Examined Patent Publication No. SHO 52(1977)-10150

[Patent Document 3] Japanese Examined Patent
20 Publication No. SHO 58(1983)-53003

[Patent Document 4] Japanese Unexamined Patent Publication No. SHO 62(1987)-59642

[Patent Document 5] Japanese Patent No. 2668384

[Disclosure of Invention]

[Problems that the Invention is to solve]

However, an expanded molded article formed with the non-crosslinked linear low-density polyethylene-based resin
5 obtained by using the Ziegler-Natta catalyst employed in the above patent is inadequate for use in, for example, cushioning and auto-parts such as interior furnishings, bumper and the like which need to have impact resistance, and it cannot achieve higher impact resistance.

10 In the above-mentioned methods, an inorganic nucleating agent is not used in the polyethylene-based resin. In the modified resin beads obtained from such resin, styrene-based resin can be dispersed in particulate form near surface regions of the beads. However, it is difficult to
15 disperse the styrene-based resin in particulate form in center regions of the beads, and the styrene-based resin would be the continuous phase as in the case of Comparative Example 1 described below. Thus, high impact resistance cannot be achieved.

20

[Means of solving the Problems]

According to one aspect, the present invention provides styrene-modified linear low-density polyethylene-based resin beads from which an expanded
25 molded article having extremely high strength is made.

The inventors of the present invention made an extensive study based on their acquaintance that it is necessary to disperse styrene-based resin in particulate form in center regions of the beads. As a result of that, the
5 inventors found that employing linear low-density polyethylene-based resin that has been polymerized using a metallocene compound as a catalyst and adding a styrene-based monomer to beads of this resin, followed by polymerization at a temperature higher than a crystallization
10 peak temperature of these beads by 10°C-35°C would allow the styrene-based resin to be dispersed in particulate form not only near the surfaces of the beads but also in the center regions of the beads. The inventors also found that the beads thus obtained can provide styrene-modified linear low-density
15 polyethylene-based resin beads from which the expanded molded article that sufficiently exhibit the impact resistance of polyethylene-based resin and the stiffness of styrene-based resin can be made.

According to one aspect of the present invention, there
20 is provided a method for producing styrene-modified linear low-density polyethylene-based resin beads, comprising the steps of: dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and
25 contain an inorganic nucleating agent, 50 to 800 parts by

weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into an aqueous suspension containing a dispersant; impregnating the
5 polyethylene-based resin beads with the styrene-based monomer under heating the resulting dispersion at such a temperature that the styrene-based monomer does not substantially polymerize; and performing polymerization of the styrene-based monomer at a temperature of $(T + 10)$ to $(T +$
10 $35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a crystallization peak temperature of the polyethylene-based resin beads).

According to another aspect of the invention, there is provided a method for producing styrene-modified linear low-density polyethylene-based resin beads, comprising the
15 steps of: dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and contain an inorganic nucleating agent, 30 to 300 parts by weight of a styrene-based monomer and 0.1 to 0.9 parts by
20 weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into an aqueous suspension containing a dispersant; impregnating the polyethylene-based resin beads with the styrene-based monomer under heating the resulting dispersion at such a
25 temperature that the styrene-based monomer does not

substantially polymerize; performing first polymerization of the styrene-based monomer at a temperature of $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a crystallization peak temperature of the polyethylene-based resin beads); and subsequent to the first
5 polymerization, adding a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer and adjusting the temperature of the resulting dispersion to $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a crystallization peak temperature of the
10 polyethylene-based resin beads), so that impregnation of the low-density polyethylene-based resin beads with the styrene-based monomer and second polymerization take place, wherein the total amount of the styrene-based monomers used in the first and second polymerization is 50 to 800 parts by
15 weight relative to 100 parts by weight of the polyethylene-based resin beads.

Furthermore, there is provided a method for producing styrene-modified linear low-density polyethylene-based expandable resin beads, comprising the steps of: dispersing
20 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and contain an inorganic nucleating agent, 50 to 800 parts by weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization
25 initiator relative to 100 parts by weight of the styrene-based

monomer into an aqueous suspension containing a dispersant;
impregnating the polyethylene-based resin beads with the
styrene-based monomer under heating the resulting dispersion
at such a temperature that the styrene-based monomer does
5 not substantially polymerize; performing polymerization of the
styrene-based monomer at a temperature of $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a crystallization peak temperature of the
polyethylene-based resin beads); and impregnating the resin
beads during or after the polymerization with a volatile blowing
10 agent.

Still further, there is provided a method for producing
styrene-modified linear low-density polyethylene-based
expandable resin beads, comprising the steps of: dispersing
100 parts by weight of non-crosslinked linear low-density
15 polyethylene-based resin beads which are polymerized using a
metallocene compound as a catalyst and contain an inorganic
nucleating agent, 30 to 300 parts by weight of a styrene-based
monomer and 0.1 to 0.9 parts by weight of a polymerization
initiator relative to 100 parts by weight of the styrene-based
20 monomer into an aqueous suspension containing a dispersant;
impregnating the polyethylene-based resin beads with the
styrene-based monomer under heating the resulting dispersion
at such a temperature that the styrene-based monomer does
not substantially polymerize; performing first polymerization of
25 the styrene-based monomer at a temperature of $(T + 10)$ to $(T +$

35)°C (where T°C is a crystallization peak temperature of the polyethylene-based resin beads); subsequent to the first polymerization, adding a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer and adjusting the temperature of the resulting dispersion to (T + 10) to (T + 35)°C (where T°C is a crystallization peak temperature of the polyethylene-based resin beads), so that impregnation of the polyethylene-based resin beads with the styrene-based monomer and second polymerization take place, wherein the total amount of the styrene-based monomers used in the first and second polymerization is 50 to 800 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads; and impregnating the resin beads during or after the polymerization with a volatile blowing agent.

In accordance with the present invention, provided is styrene-modified linear low-density polyethylene-based resin beads, comprising 50 to 800 parts by weight of styrene-based resin relative to 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin which is polymerized using a metallocene compound as a catalyst, wherein styrene-based resin is dispersed a form particles in a beads, and the particle diameter is 0.8 μm or smaller in a surface region within at least 5 μm from the bead surface and a center region within about a 5 μm radius from the bead center.

In accordance with the present invention, also provided is styrene-modified linear low-density polyethylene-based resin beads, comprising a volatile blowing agent and 50 to 800 parts by weight of styrene-based resin relative to 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin which is polymerized using a metallocene compound as a catalyst, wherein styrene-based resin is dispersed a form particles in a beads, and the particle diameter is 0.8 μm or smaller in a surface region within at least 5 μm from the bead surface and a center region within about a 5 μm radius from the bead center.

Furthermore, the present invention provides pre-expanded beads having a bulk density of 10 to 300 kg/m^3 obtained by pre-expanding the above-mentioned styrene-modified linear low-density polyethylene-based expandable resin beads.

Still further, the present invention provides an expanded molded article having a density of 10 to 300 kg/m^3 obtained by expansion molding of the above-mentioned pre-expanded beads.

[Effect of the Invention]

In the present invention, as described above, the step of impregnating the polyethylene-based resin beads, which are polymerized using a metallocene compound as a catalyst and

contain an inorganic nucleating agent, with the styrene-based monomer to perform polymerization is carried out at a specific temperature. This allows for production of the modified resin beads in which the styrene-based particles are dispersed in
5 particulate form not only near the surface but also near the center of the beads. Furthermore, the styrene-modified linear low-density polyethylene-based resin beads and styrene-modified linear low-density polyethylene-based expandable resin beads excellent in physical properties,
10 particularly in impact resistance, can be provided. The present invention also has an advantage that the expandable beads that generates a smaller amount of polymer powder and has a high styrene-based resin content can be provided. Such expandable beads can be provided by impregnating the inside
15 of the polyethylene-based resin beads with the styrene-based monomer to polymerize the styrene-based monomer, and then adding additional styrene-based monomer after the polymerization has proceeded to a certain degree, so that the impregnation and polymerization take place simultaneously at
20 a specific temperature.

[Brief Description of Drawings]

Fig. 1 is a TEM picture showing a surface region cross-section of a modified resin bead according to Example 1
25 of the present invention;

Fig. 2 is a TEM picture showing a center region cross-section of the modified resin bead according to Example 1 of the present invention;

Fig. 3 is a TEM picture showing a surface region cross-section of a modified resin bead according to Example 2 of the present invention;

Fig. 4 is a TEM picture showing a center region cross-section of the modified resin bead according to Example 2 of the present invention;

Fig. 5 is a view in which the TEM picture of Fig. 4 is traced;

Fig. 6 is a TEM picture showing a surface region cross-section of a modified resin bead according to Comparative Example 1;

Fig. 7 is a TEM picture showing a center region cross-section of the modified resin bead according to Comparative Example 1;

Fig. 8 is a TEM picture showing a surface region cross-section of a modified resin bead according to Comparative Example 7; and

Fig. 9 is a TEM picture showing a center region cross-section of the modified resin bead according to Comparative Example 7.

[Best Mode for Carrying Out the Invention]

Styrene-modified linear low-density
polyethylene-based resin beads (hereinafter referred to as
modified resin beads) obtained by the production method of the
present invention are beads made of base resin in which
5 styrene-based resin is dispersed in particulate form. In other
words, the modified resin beads are made of base resin in
which non-crosslinked linear low-density polyethylene-based
resin beads (hereinafter simply referred to as
polyethylene-based resin beads) containing an inorganic
10 nucleating agent and being polymerized using a metallocene
compound as a catalyst are impregnated with a styrene-based
monomer to polymerize the styrene-based monomer.
Furthermore, styrene-modified linear low-density
polyethylene-based expandable resin beads (hereinafter
15 referred to as expandable beads) are beads in which a volatile
blowing agent is contained in the base resin.

The polyethylene-based resin beads used in the
present invention are beads containing the inorganic
nucleating agent and polyethylene-based resin polymerized
20 using a metallocene compound as a catalyst.

As the metallocene compound, known metallocene
compounds which are employed in polymerization of
ethylene-based monomers can be used. For example, a
metallocene compound having a tetravalent transition metal
25 can be suitably used. More specifically, there can be used

cyclopentadienyl titanium tris(dimethylamide),
methylcyclopentadienyl titanium tris(dimethylamide),
bis(cyclopentadienyl) titanium dichloride,
dimethylsilyltetramethylcyclopentadienyl-t-butylamide
5 zirconium dichloride,
dimethylsilyltetramethylcyclopentadienyl-t-butylamide hafnium
dichloride, dimethylsilyltetramethylcyclopentadienyl-p-n-
butylphenylamide zirconium chloride,
methylphenylsilyltetramethylcyclopentadienyl-t-butylamide
10 hafnium dichloride, indenyl titanium tris(dimethylamide),
indenyl titanium tris(diethylamide), indenyl titanium tris
(di-n-propylamide), indenyl titanium bis(di-n-butylamide),
indenyl titanium bis(di-n-propylamide) and/or the like. These
metallocene compounds having a tetravalent transition metal
15 may be used alone or two or more of these may be used in
combination. Alternatively, the metallocene compound may
be used together with a cocatalyst such as methylaluminoxane,
a boron-based compound or the like.

As the polyethylene-based resin, a homopolymer of
20 ethylene, a copolymer of ethylene and an α -olefin or the like
can be used.

As the α -olefin, propylene, 1-butene, 1-pentene,
1-hexene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene,
4,4-dimethyl-1-pentene, 1-heptene, 1-octene and/or the like
25 can be used. Among these, 1-butene and 1-hexene are

preferred. These α -olefins may be used alone or two or more of these may be used in combination.

The ratio of ethylene to α -olefin may appropriately vary depending on the desired properties, and preferably is in
5 the range of 1:0.01 to 1:0.1 (in weight). By "low-density", a density in the range of about 0.910 g/ml to 0.925 g/ml is meant.

Polymerization of the polyethylene-based resin is carried out using the metallocene compound as the catalyst.
10 For the ethylene homopolymer, for example, vapor-phase polymerization can be employed and for the ethylene/ α -olefin copolymer, for example, solution polymerization using an inert medium, bulk polymerization and vapor-phase polymerization which are substantially free of an inert medium can be
15 employed.

The polyethylene-based resin preferably has a molecular weight distribution (M_w/M_n) of 1.5 to 3.5 measured by GPC (Gel Permeation Chromatography). This range of molecular weight distribution allows for easier molding and an
20 improvement in strength (particularly, in impact resistance) of the resulting molded articles.

As the non-crosslinked linear polyethylene-based resin which is polymerized using the metallocene compound as the catalyst, there can be used the FMRN series manufactured by
25 Nippon Unicar Company Limited, the Evolue F series

manufactured by Sumitomo Chemical Co. Ltd., the Evolve series manufactured by Mitsui Chemicals, Inc., the AFFINITY PL series manufactured by Dow Chemical Company or the like.

Together with the above, other polymers and
5 copolymers may be used in such a range that the desired effects of the present invention are not hindered. Specific examples of such polymers and copolymers include low-density polyethylene, high-density polyethylene, an ethylene/propylene copolymer, an ethylene/vinyl acetate copolymer and an
10 ethylene/acrylic acid copolymer having a crosslink and/or a branched chain, and a combination of two or more of these.

As an inorganic nucleating agent, for example, talc, silica, mica, clay, zeolite, calcium carbonate or the like can be used.

15 The amount of the inorganic nucleating agent used is preferably 0.1 to 2 parts by weight, and more preferably 0.2 to 1.5 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads. An amount less than 0.1 parts by weight is not preferred because it would be difficult to
20 diffuse the styrene-based resin in the polyethylene-based resin so as to make the styrene-based resin be in the form of particles of 0.8 μm or smaller. An amount more than 2 parts by weight is not preferred because the strength of the expanded molded article would tend to decrease.

25 Furthermore, additives such as a coloring material

(colorant), a fire retardant, an antioxidant, an ultraviolet absorber and the like may be contained in the polyethylene-based resin beads upon necessity.

As the coloring material, both inorganic and organic
5 coloring materials can be used. Particularly, inorganic coloring materials such as iron oxide, carbon black and the like are preferred.

As the iron oxide, there can be used α -FeOOH (water-containing crystal) as iron oxide yellow, α -Fe₂O₃ as iron
10 oxide red, (FeO)_x(Fe₂O₃)_y as iron oxide black or the like. These iron oxides may have another metal such as Zn, Mg or the like substituting for a part of Fe. Furthermore, the iron oxides may be mixed to obtain a desired color. Among the above iron oxides, Fe₃O₄ included in iron oxide black,
15 (FeO)_x(Fe₂O₃)_y, is preferred.

The iron oxide preferably has an average particle diameter of 0.1 μ m to 1 μ m, and more preferably an average particle diameter of 0.2 μ m to 0.8 μ m. The average particle diameter can be measured with a laser diffraction particle size
20 analyzer (RODOS manufactured by JEOL Ltd.)

The polyethylene-based resin beads contain the iron oxide preferably in the range of 1.5 wt% to 70 wt%, more preferably in the range of 5 wt% to 40 wt%, and still more preferably in the range of 10 wt% to 30 wt%. An amount less
25 than 1.5 wt% is not preferred because the polyethylene-based

resin beads may not be adequately colored. An amount more than 70 wt% is not preferred because it would be difficult to mix the iron oxide with the polyethylene-based resin beads. Furthermore, because the specific gravity of the iron oxide is greater than that of the polyethylene-based resin, an amount more than 70 wt% would increase the weight of the resin beads and the resin beads would not be uniformly impregnated with the styrene-based monomer.

As the carbon black, furnace black, channel black, thermal black, acetylene black, graphite, carbon fiber or the like can be used.

The polyethylene-based resin beads contain the carbon black preferably in the range of 1 wt% to 50 wt%, and more preferably in the range of 2 wt% to 30 wt%. An amount less than 1 wt% is not preferred because the polyethylene-based resin beads may not be adequately colored. An amount more than 50 wt% is not preferred because it would be difficult to mix the carbon black with the polyethylene-based resin beads.

Examples of the styrene-based resin include those of monomer origin such as styrene, α -methyl styrene, vinyltoluene, chlorostyrene and the like.

The amount of styrene-based resin is 50 to 800 parts by weight, and preferably 100 to 700 parts by weight relative to 100 parts by weight of the polyethylene-based resin. Where

the amount of styrene-based resin is less than 50 parts by weight, it is difficult to show the characteristic of the styrene-based resin, namely, high stiffness. Where the amount of styrene-based resin is more than 800 parts by weight, it is difficult to show the characteristics of the polyethylene-based resin, namely, high elasticity and high oil and impact resistance. Furthermore, the styrene-based monomer cannot be sufficiently absorbed into the inside of the polyethylene-based resin, causing polymer powder in which the styrene-based monomer is polymerized by itself to be generated.

In the case of expandable beads, an amount of styrene-based resin less than 50 parts by weight makes the retention of the volatile blowing agent extremely poor, rendering it difficult to achieve low density. This also renders the expansion molding more difficult.

Particularly, with the styrene-based resin in an amount of 300 parts by weight or more, it is difficult to provide modified resin beads and expandable beads uniformly containing the styrene-based resin by conventional methods. The present invention, on the other hand, can provide such resin beads.

As the volatile blowing agent, for example, hydrocarbons such as propane, n-butane, isobutane, pentane, isopentane, cyclopentane, hexane and the like can be used

alone or two or more of these hydrocarbons can be used in combination.

The content of the blowing agent is preferably 5 to 20 parts by weight relative to 100 parts by weight of resin that
5 makes up the expandable beads (the sum of the polyethylene-based resin and the styrene-based resin).

Preferably, the modified resin beads and the expandable beads each have a cylindrical, spherical or substantially spherical shape with a L/D (where L is a length
10 of the bead and D is a mean diameter of the bead) of 0.6 to 1.6. The average size of the beads is preferably 0.3 mm to 3.0 mm.

The beads having a L/D smaller than 0.6 or greater than 1.6, that is, the beads having high ovality are not preferred because it would be difficult to fill pre-expanded
15 beads obtained from such modified resin beads and expandable beads into a mold when forming an expanded molded article.

The shape of the beads preferably is spherical or substantially spherical so as to make the filling easier.

20 An average bead size smaller than 0.3 mm is not preferred because the retention of the blowing agent would decrease and the reduction in density would tend to be difficult. An average bead size greater than 3.0 mm is not preferred because not only the filling into a mold would be difficult, but
25 thinning of an expanded molded article would also be difficult.

According to the present invention, there can be provided the modified resin beads and expandable beads. Each of these beads, when seen in cross-section, has the styrene-based resin dispersed in the form of particles of a predetermined size in the polyethylene-based resin as described below.

In other words, there can be provided the modified resin beads and expandable beads each having the styrene-based resin dispersed in particulate form in the polyethylene-based resin in a surface region and a center region of the bead. The surface region is an area within at least 5 μm from the surface of each bead and the center region is an area within a 5 μm radius from the center of the bead. It is not preferable that the styrene-based resin in particulate form forms the continuous phase and thereby the particle diameter exceeds 0.8 μm as shown in the cross-sectional pictures of the bead center regions of Comparative Examples 1 and 7, because a remarkable improvement in impact resistance would not be achieved. The styrene-based resin is dispersed in the form of particles having a diameter of 0.8 μm or smaller, and preferably 0.6 μm or smaller in the polyethylene-based resin. The lower limit for the particle diameter of the styrene-based resin in particulate form (hereinafter referred to as styrene-based resin particles) is about 0.01 μm . As described above, the styrene-based resin can be dispersed in

particulate form in the surface and center regions of each bead.

The diameter of the styrene-based resin particles in the surface region of each bead is preferably 0.01 μm to 0.8 μm , more preferably 0.01 μm to 0.6 μm , and still more preferably 0.03 μm to 0.4 μm . On the other hand, the diameter of the styrene-based resin particles in the center region of each bead is preferably 0.01 μm to 0.8 μm , more preferably 0.01 μm to 0.6 μm , and still more preferably 0.05 μm to 0.55 μm .

Next, a production method of the modified resin beads and expandable beads according to the present invention will be described.

In an aqueous suspension containing a dispersant, 100 parts by weight of polyethylene-based resin beads, 50 to 800 parts by weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer are dispersed. Here, the styrene-based monomer and the initiator may be mixed in advance.

As an aqueous medium that makes up the aqueous suspension, there can be used water or a mixed medium of water and a water-soluble solvent (for example, lower alcohol).

The dispersant is not particularly limited, and any of the known dispersants can be used. More specifically, there

can be used slightly soluble inorganic substances such as calcium phosphate, magnesium pyrophosphate, sodium pyrophosphate, magnesium oxide and the like. Furthermore, a surface-active agent such as sodium dodecylbenzene-sulfonate may be used.

The polyethylene-based resin beads can be obtained by known methods. For example, there is a method in which polyethylene-based resin and an inorganic nucleating agent together with an additive, if necessary, are melted and kneaded in an extruder and then extruded from the extruder to obtain a strand. Then, the obtained strand is cut in the air or in the water or cut while being heated to granulate the strand.

Preferably, the polyethylene-based resin beads each have a cylindrical, spherical or substantially spherical shape with an L/D (where L is a length of the bead and D is a mean diameter of the bead) of 0.6 to 1.6. The average size of the beads is preferably 0.2 mm to 1.5 mm. The beads having a L/D smaller than 0.6 or greater than 1.6, that is, the beads having high ovality are not preferred because it would be difficult to fill pre-expanded beads of expandable beads into a mold when forming an expanded molded article. The shape of the beads is preferably spherical or substantially spherical so as to make the filling easier. An average bead size smaller than 0.2 mm is not preferred because the retention of the blowing agent would decrease and the reduction in density

would tend to be difficult. An average bead size greater than 1.5 mm is not preferred because not only the filling into a mold would be difficult, but thinning of an expanded molded article would also be difficult.

5 As the polymerization initiator, those typically used as a polymerization initiator for suspension polymerization of a styrene-based monomer can be used. Examples thereof include organic peroxides such as di-t-butyl peroxide, t-butyl peroxy benzoate, dicumyl peroxide,
10 2,5-dimethyl-2,5-di-t-butylperoxy hexane, t-butylperoxy-3,5,5-trimethyl hexanoate, t-butyl-peroxy-2-ethylhexyl carbonate and the like. These initiators may be used alone or two or more of these may be used in combination.

15 The amount of the initiator used is preferably 0.1 to 0.9 parts by weight and more preferably 0.2 to 0.5 parts by weight relative to 100 parts by weight of the styrene-based monomer. An amount less than 0.1 parts by weight is not preferred because too much time would be required for the
20 polymerization of the styrene-based monomer. An amount more than 0.9 parts by weight is not preferred because the molecular weight of the styrene-based resin would decrease, and thereby the impact resistance would be reduced.

 In order to achieve excellent properties, the molecular
25 weight of the styrene-based resin is preferably about two

hundred thousands to about five hundred thousands.

However, where more than 0.9 parts by weight of the initiator is used, only a molecular weight smaller than the above-mentioned range can be obtained.

5 50 to 800 parts by weight of the styrene-based monomer relative to 100 parts by weight of the polyethylene-based resin beads is added and dispersed preferably under stirring, and the resulting dispersion is heated to such a temperature that the styrene-based monomer
10 does not substantially polymerize so that the polyethylene-based resin beads are impregnated with the styrene-based monomer.

 The time appropriate for sufficiently impregnating the inside of the polyethylene-based resin beads with the
15 styrene-based monomer is 30 minutes to 3 hours. Where polymerization takes place before the beads are sufficiently impregnated, polymer powder of the styrene-based resin is generated. It is desirable that the generation of polymer powder is prevented. It is advantageous that the temperature
20 at which the monomer does not substantially polymerize is as high as possible to accelerate the impregnation rate, but it needs to be determined with consideration given to the decomposition temperature of the initiator.

 Next, polymerization of the styrene-based monomer is
25 carried out at a temperature of $(T + 10) ^\circ\text{C}$ to $(T + 35) ^\circ\text{C}$ where

T°C is the crystallization peak temperature of the polyethylene-based resin beads.

A polymerization temperature lower than $(T + 10)^{\circ}\text{C}$ is not preferred because the styrene-based resin would not be
5 dispersed in particulate form near the center regions of modified resin beads and the styrene-based resin would be the continuous phase. Furthermore, a polymerization temperature higher than $(T + 35)^{\circ}\text{C}$ is not preferred because aggregated particles in which particles coalesce would be
10 generated.

With the above steps, the modified resin beads can be obtained. The expandable beads can be obtained by impregnating the modified resin beads during or after the polymerization with the volatile blowing agent. The
15 impregnation can be carried out by per se known methods. For example, the impregnation during the polymerization can be carried out by making polymerization reaction to occur in a closed vessel and injecting the volatile blowing agent into the vessel. The impregnation after the polymerization can be
20 carried out by injecting the volatile blowing agent into a closed vessel.

Thus, the modified resin beads and expandable beads having excellent characteristics can be provided by the above-mentioned methods. However, where the amount of
25 styrene-based monomer exceeds 300 parts by weight relative to

100 parts by weight of the polyethylene-based resin beads,
polymer powder of the styrene-based monomer tends to
increase in amount.

In other words, when the amount of styrene-based
5 monomer is 50 to 300 parts by weight relative to 100 parts by
weight of the polyethylene-based resin, the amount of polymer
powder of styrene-based resin is small and the modified resin
beads and expandable beads having the most stable, excellent
characteristics can be easily provided.

10 Where the amount of styrene-based monomer exceeds
300 parts by weight, it is preferable that the
polyethylene-based resin beads are impregnated with the
styrene-based monomer in two separate steps as described
below in order to reduce the generation of polymer powder.

15 In an aqueous suspension containing a dispersant,
100 parts by weight of polyethylene-based resin beads, 30 to
300 parts by weight of a styrene-based monomer and 0.1 to 0.9
parts by weight of a polymerization initiator relative to 100
parts by weight of the styrene-based monomer are dispersed.
20 Here, the styrene-based monomer and the initiator may be
mixed in advance.

Then, the resulting dispersion is heated to such a
temperature that the styrene-based monomer does not
substantially polymerize to impregnate the polyethylene-based
25 resin beads with the styrene-based monomer.

Subsequently, first polymerization of the styrene-based monomer is carried out at a temperature of $(T + 10) ^\circ\text{C}$ to $(T + 35) ^\circ\text{C}$ where $T^\circ\text{C}$ is the crystallization peak temperature of the polyethylene-based resin beads.

5 Next, a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer are added to the reaction solution of the first polymerization, and the temperature is adjusted to $(T + 10) ^\circ\text{C}$ to $(T + 35) ^\circ\text{C}$ where $T^\circ\text{C}$ is the
10 crystallization peak temperature of the polyethylene-based resin beads, so that impregnation of the low-density polyethylene-based resin beads with the styrene-based monomer and second polymerization take place. The total amount of the styrene-based monomers used in the first and
15 second polymerization is 50 to 800 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads. The styrene-based monomer and the initiator may be mixed in advance.

 The second addition of the styrene-based monomer
20 and the initiator may be continuous or intermittent. In order to effectively prevent the generation of polymer powder, it is preferable that the impregnation of the inside of the polyethylene-based resin beads and the polymerization take place at approximately the same time. Because the
25 polymerization is carried out at a relatively high temperature,

a too high addition rate is not preferred. If the addition rate is too high, the polymerization would proceed before the impregnation takes place. For example, the addition rate is preferably 30 to 100 parts by weight/hour.

5 With the above steps, the modified resin beads can be obtained. The expandable beads can be obtained as described above by impregnating the resin beads during or after the polymerization with the volatile blowing agent. The impregnation can be carried out by per se known methods
10 such as the one described in Examples.

 The expandable beads can be formed into pre-expanded beads by pre-expanding the expandable beads to a predetermined bulk density (for example, 10 to 300 kg/m³) by known methods. The method of measuring the bulk
15 density will be described in Examples.

 Furthermore, an expanded molded article can be provided by filling the pre-expanded beads into a mold, and while heating again to expand the pre-expanded beads, heat fusing the expanded beads.

20 Steam is suitably used as a medium for heating. The expanded molded article preferably has a density of 10 to 300 kg/m³. A density lower than 10 kg/m³ is not preferred because sufficient strength would not be achieved. A density higher than 300 kg/m³ is not preferred because a reduction in
25 weight cannot be achieved and elasticity, which is one of the

characteristics of the polyethylene-based resin expanded molded article, may not be sufficiently exhibited.

The obtained expanded molded article is strong and particularly excellent in impact resistance. Since the molded
5 article is modified with the styrene-based resin, it also has high stiffness.

The expanded molded article according to the present invention can be used for various purposes, and is particularly suitable for use in interior of cars, energy absorbing material
10 inserted inside bumpers, packing material for heavy products, and the like.

Since the present invention employs as polyethylene-based resin the resin using a metallocene compound as a catalyst, it can provide an expanded molded
15 article having a falling ball impact value of 80 cm or greater. Although a molded article having a falling ball impact value of less than 80 cm can be used, the one with a value of 80 cm or greater does not easily suffer from cracking and chipping and can suitably be used particularly for energy absorbing
20 materials. A falling ball impact value of 90 cm or greater is more preferred. A method for measuring the falling ball impact resistance will be described in Examples.

[Examples]

25 The present invention will hereinafter be described by

way of Examples thereof. It should be understood that the invention be not limited to these Examples. The measurement methods of various values adopted in Examples and Comparative Examples will also be described below.

5 [Measurement of crystallization peak temperature of polyethylene-based resin]

The crystallization peak temperature is measured according to JIS K7121 using a differential scanning calorimeter (DSC). More specifically, resin as a measurement
10 sample is set on a measuring vessel of the DSC, and the temperature is raised to 280°C at a heating rate of 10°C/min. After being kept at 280°C for 10 min., the resin is left to cool to a room temperature (23°C) and the crystallization peak temperature is measured while the temperature of the resin is
15 raised again at a heating rate of 10°C/min.

[Measurement of melt flow rate of polyethylene-based resin]

The melt flow rate is measured at 230°C under a load of 10 kgf according to JIS K7210.

[Measurement of polyethylene-based resin density]

20 The density is measured according to JIS K6992-2.

[Measurement of molecular weight distribution: Mw/Mn]

The measurement is carried out using a GPC under the following conditions.

Instrument: GPC instrument Type 150C manufactured by

25 Nihon Waters K.K.

Column: TSK GMH-6 manufactured by TOSOH Corporation

Solvent: ortho-dichlorobenzene (ODCB)

Temperature: 135°C

Flow rate: 1 ml/min.

- 5 Injection concentration: 10 mg/10 ml ODCB (injection amount:
500 µl)

The weight-average molecular weight M_w and the
number-average molecular weight M_n are determined by
conversion from the calibration curve using standard styrene
10 resin, and then the M_w/M_n is calculated.

[Measurement of bulk density]

The measurement is carried out according to a
method described in JIS K 6911:1995 "General testing methods
for thermosetting plastics". More specifically, pre-expanded
15 beads are allowed to free fall into a graduated cylinder and
their weight is measured by an apparent density measuring
instrument. The bulk density is determined from the
following equation.

bulk density (kg/m³) = weight (kg)/beads volume in graduated cylinder (m³)

- 20 [Measurement of expanded molded article density]

The density of an expanded molded article is measured
by a method described in JIS A 9511:1995 "Prefoamed cellular
plastics thermal insulation materials".

[Measurement of Impact strength]

- 25 For the measurement of the impact strength, a sample

having a size of 215 mm x 40 mm x 20 mm is cut from the expanded molded article. The sample is then placed on a pair of holding members arranged at a distance of 155 mm. A steel ball weighing 321 g is dropped from a predetermined
5 height on a position at the center of the sample in width direction and at a halfway between the pair of holding members to see whether or not the sample is broken.

This test is repeated from a variety of ball-drop heights and the minimum height that produced a break in the
10 sample is defined as a falling ball impact value. The impact strength is thus evaluated. The impact strength increases as the falling ball impact value increases.

The maximum height from which the ball is dropped is set to 120 cm. Where the falling ball impact value exceeds
15 120 cm, the weight of the ball is changed to 534 g or 1044 g and the falling ball impact value is measured in the same manner as described above. The obtained value is converted into a falling ball impact value of the ball of 321 g by the following equation.

- 20 (1) impact value of 321 g ball = $(534/321) \times (\text{impact value of 534 g ball})$
(2) impact value of 321 g ball = $(1044/321) \times (\text{impact value of 1044 g ball})$

In Examples and Comparative Examples, where the falling ball impact value is greater than 120 cm and smaller than 200 cm, values converted by the above equation (1) are
25 shown, and where the falling ball impact value is greater than

200 cm, values converted by the above equation (2) are shown.

Example 1

As a non-crosslinked linear low-density
5 polyethylene-based resin, LLDPE synthesized by using a
metallocene catalyst (manufactured by Nippon Unicar
Company Limited, tradename: FMRN-063, crystallization peak
temperature: 101°C, melt flow rate: 1.3g/10 min., density:
0.914 g/cm³, molecular weight distribution (Mw/Mn): 2.77)
10 was employed. 100 parts by weight of LLDPE and 0.5 parts by
weight of talc were fed into an extruder. The feedstock was
melted and kneaded, and then granulated by under water cut
system to provide oval (egg-shaped) polyethylene-based resin
beads. The average weight of the polyethylene-based resin
15 beads was 0.6 mg.

Next, 0.8 parts by weight of magnesium pyrophosphate
(dispersant) and 0.02 parts by weight of sodium
dodecylbenzenesulfonate (surface-active agent) were dispersed
in 100 parts by weight of water to obtain a medium for
20 dispersion.

In the dispersion medium, 100.5 parts by weight of the
polyethylene-based resin beads were dispersed to obtain a
suspension.

0.19 parts by weight of dicumyl peroxide as a
25 polymerization initiator was dissolved in advance in 100 parts

by weight of a styrene monomer.

The temperature of the dispersion of the polyethylene-based resin beads was adjusted to 60°C and the styrene-based monomer containing the initiator was added
5 quantitatively to the dispersion over 30 min. Then, the resulting mixture was stirred at 60°C for an hour to impregnate the polyethylene-based resin beads with the styrene monomer.

Next, the temperature of the dispersion was raised to
10 130°C and kept for 2 hours to polymerize the styrene monomer in the polyethylene-based resin beads. Thus, modified resin beads were obtained.

The dispersion state of the styrene resin in the obtained modified resin beads was observed by a TEM
15 (transmission electron microscope). The styrene resin particles with a particle diameter of 0.04 μm to 0.2 μm were dispersed in a surface region (x22,500, an area within about 5 μm from the surface) and the styrene resin particles with a particle diameter of 0.05 μm to 0.5 μm were dispersed in a
20 center region (x12,800, an area within about a 5 μm radius from the center). The cross-sectional pictures of the surface region and the center region are shown in Fig. 1 and Fig. 2, respectively.

Subsequently, 100 parts by weight of the modified
25 resin beads, 0.15 parts by weight of monoglyceride stearate

and 0.5 parts by weight of diisobutyl adipate were fed into a pressure-resistant V-type rotary mixer having a volume of 1m³, and 14 parts by weight of butane (n-butane: i-butane = 7:3) as a volatile blowing agent was injected at a normal temperature
5 while the mixer was rotated. After the temperature was raised to 70°C and kept for 4 hours, it was cooled to 25°C to obtain expandable beads. The obtained expandable beads had styrene resin particles with a particle diameter of 0.04 μm to 0.2 μm dispersed in a surface region and styrene resin
10 particles with a particle diameter of 0.05 μm to 0.5 μm dispersed in a center region as in the case of the modified resin beads.

The obtained expandable beads were immediately introduced into a pre-expanding machine and steam was
15 introduced at a pressure of 0.02 MPa to pre-expand the beads. Pre-expanded beads having a bulk density of 60 kg/m³ were obtained.

Then, the pre-expanded beads were filled into a mold of a foam molding machine, and then steam was introduced for
20 expansion molding of the pre-expanded beads. A rectangular parallelepiped expanded molded article having a bulk density of 60 kg/m³ and a size of 300 mm x 400 mm x 50 mm was obtained. The falling ball impact value of the obtained molded article was measured and it was as excellent as 250.5 cm.

Example 2

100.5 parts by weight of polyethylene-based resin beads obtained in the same manner as in Example 1 were dispersed in a dispersion medium obtained in the same
5 manner as in Example 1.

Furthermore, 0.19 parts by weight of dicumyl peroxide as a polymerization initiator was dissolved in advance in 66 parts by weight of a styrene monomer to obtain a first styrene monomer.

10 The temperature of the dispersion of the polyethylene-based resin beads was adjusted to 60°C and the first styrene monomer containing the initiator was added quantitatively to the dispersion over 30 min. Then, the resulting mixture was stirred at 60°C for an hour to
15 impregnate the polyethylene-based resin beads with the first styrene monomer.

Next, the temperature of the dispersion was raised to 130°C and kept for two hours to polymerize (first polymerization) the first styrene monomer in the
20 polyethylene-based resin beads.

Subsequently, 0.3 parts by weight of dicumyl peroxide as a polymerization initiator was dissolved in 534 parts by weight of a styrene monomer to obtain a second styrene monomer. The second styrene monomer was dropped
25 continuously into the reaction solution of the first

polymerization at a rate of 80 parts by weight per hour for 7 hours, so that the second styrene monomer was polymerized (second polymerization) while the polyethylene-based resin beads were impregnated with the monomer to obtain modified
5 resin beads.

The dispersion state of the styrene resin in the obtained modified resin beads was observed by the TEM (transmission electron microscope). The styrene resin particles with a particle diameter of 0.05 μm to 0.35 μm were
10 dispersed in a surface region ($\times 19,300$, an area within about 5 μm from the surface) and the styrene resin particles with a particle diameter of 0.06 μm to 0.4 μm were dispersed in a center region ($\times 38,600$, an area within about a 5 μm radius from the center). The cross-sectional pictures of the surface
15 region and the center region are shown in Fig. 3 and Fig. 4, respectively.

Subsequently, expandable beads were prepared in the same manner as in Example 1 except that the amount of blowing agent was changed to 12 parts by weight, 14 parts by
20 weight and 16 parts by weight. The obtained expandable beads had styrene resin particles with a particle diameter of 0.05 μm to 0.35 μm dispersed in a surface region and styrene resin particles with a particle diameter of 0.06 μm to 0.4 μm dispersed in a center region as in the case of the
25 above-mentioned modified resin beads.

An expanded molded article was obtained in the same manner as in Example 1 and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m³ (the amount of blowing agent: 14 parts by weight) was as excellent as 175.5 cm. Molded articles respectively having a density of 30 kg/m³ (the amount of blowing agent: 16 parts by weight) and 150 kg/m³ (the amount of blowing agent: 12 parts by weight) were prepared and the falling ball impact values were measured. The values of the molded articles were as excellent as 105.5 cm and 260.5 cm, respectively.

The diameter of the styrene resin particles in the surface region and the center region were determined as follows. The particles of Fig. 4, for example, were traced as shown in Fig. 5 in such a manner that the areas of the particles of the two figures are substantially equal. The diameter of each particle was measured from the tracing of Fig. 5 and it was confirmed that the particle diameters were in the range of 0.06 μm to 0.4 μm.

Example 3

Modified resin beads were obtained in the same manner as in Example 2 except that "Evolue F-201" manufactured by Sumitomo Chemical Co. Ltd. (melting point: 117°C, crystallization peak temperature: 108°C, melt flow rate: 1.5 g/10 min., density: 0.915 g/cm³, and molecular weight

distribution (M_w/M_n): 2.5) was employed as the linear low-density polyethylene-based resin.

The dispersion state of styrene resin in the obtained modified resin beads was observed by the TEM. The styrene resin particles with a particle diameter of 0.05 μm to 0.3 μm were dispersed in a surface region (an area within about 5 μm from the surface) and the styrene resin particles with a particle diameter of 0.1 μm to 0.5 μm were dispersed in a center region (an area within about a 5 μm radius from the center).

Next, expandable beads were obtained in the same manner as in Example 1. In the obtained expandable beads, the styrene resin particles with a particle diameter of 0.05 μm to 0.3 μm were dispersed in a surface region and the styrene resin particles with a particle diameter of 0.1 μm to 0.5 μm were dispersed in a center region as in the case of the above-mentioned modified resin beads.

An expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m^3 was as excellent as 155.5 cm.

Example 4

Into an extruder, 100 parts by weight of the same linear low-density polyethylene-based resin as that of Example 1, 25 parts by weight of iron oxide particles (Fe_3O_4) and 0.5

parts by weight of talc were fed. The feedstock was melted and kneaded, and then granulated by under water cut system to provide oval (egg-shaped) black-colored polyethylene-based resin beads. The average weight of the polyethylene-based
5 resin beads containing iron oxide was 0.7 mg.

Modified resin beads and expandable beads were obtained in the same manner as in Example 2 except that the obtained iron oxide-containing polyethylene-based resin beads were used.

10 The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM as in Example 1. The styrene resin particles with a particle diameter of 0.05 μm to 0.3 μm were dispersed in surface regions and the styrene resin particles with a particle
15 diameter of 0.1 μm to 0.45 μm were dispersed in center regions.

Next, expansion molding was carried out in the same manner as in Example 1 to obtain a molded article having a density of 60 kg/m^3 . The measured falling ball impact value
20 of this foam was as excellent as 125.5 cm.

Example 5

Oval (egg-shaped) black-colored polyethylene-based resin beads were obtained in the same manner as in Example 4
25 except that 3 parts by weight of carbon black particles were

used instead of the iron oxide particles. The average weight of the carbon black-containing polyethylene-based resin beads was 0.6 mg.

Modified resin beads were obtained in the same
5 manner as in Example 2 except that the obtained carbon black-containing polyethylene-based resin beads were used. Then, expandable beads were obtained in the same manner as in Example 1.

The dispersion states of styrene resin in the obtained
10 modified resin beads and expandable beads were observed by the TEM as in Example 1. The styrene resin particles with a particle diameter of 0.06 μm to 0.3 μm were dispersed in surface regions and the styrene resin particles with a particle diameter of 0.1 μm to 0.55 μm were dispersed in center
15 regions.

Next, expansion molding was carried out in the same manner as in Example 1 to obtain a black molded article having a density of 60 kg/m³. The measured falling ball impact value of this foam was as excellent as 155.5 cm.

20

Example 6

Modified resin beads and expandable beads were obtained in the same manner as in Example 1 except that the amounts of styrene monomer and α -methylstyrene monomer
25 were 95 parts by weight and 5 parts by weight, respectively.

The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter of 0.04 μm to 0.2 μm were dispersed in surface regions (areas
5 within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.05 μm to 0.5 μm were dispersed in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the
10 same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m^3 was as excellent as 245.5 cm.

Example 7

15 Modified resin beads were obtained in the same manner as in Example 2 except that the amounts of the first and second styrene monomers were 50 parts by weight and 350 parts by weight, respectively, t-butylperoxybenzoate was used as the polymerization initiator and the polymerization
20 temperature was 115°C. Then, expandable beads were obtained in the same manner as in Example 1 using 14 parts by weight and 16 parts by weight of the blowing agent, respectively.

The dispersion states of styrene resin in the obtained
25 modified resin beads and expandable beads were observed by

the TEM. The styrene resin particles with a particle diameter of 0.05 μm to 0.4 μm were dispersed in surface regions (areas within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.1 μm to 0.5 μm were
5 dispersed in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a
10 density of 60 kg/m^3 (amount of blowing agent: 14 parts by weight) was as excellent as 155.5 cm. Furthermore, an molded article having a density of 30 kg/m^3 (amount of blowing agent: 16 parts by weight) was prepared in the same manner as in Example 1. The falling ball impact value
15 measured of this molded article was as excellent as 120.5 cm.

Example 8

Modified resin beads were obtained in the same manner as in Example 7 except that the inorganic nucleating
20 agent added was silica, dicumyl peroxide was used as the initiator and the polymerization temperature was 140°C. Then, expandable beads were obtained in the same manner as in Example 1.

The dispersion states of styrene resin in the obtained
25 modified resin beads and expandable beads were observed by

the TEM. The styrene resin particles with a particle diameter of 0.03 μm to 0.3 μm were dispersed in surface regions (areas within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.08 μm to 0.4 μm were
5 dispersed in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a
10 density of 60 kg/m^3 was as excellent as 160.5 cm.

Example 9

Modified resin beads were obtained in the same manner as in Example 2 except that the amounts of the first
15 styrene-monomer and the second styrene-based monomer were 120 parts by weight and 80 parts by weight, respectively. Then, expandable beads were obtained in the same manner as in Example 1.

The dispersion states of styrene resin in the obtained
20 modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter of 0.04 μm to 0.3 μm were dispersed in surface regions (areas within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.05 μm to 0.5 μm were
25 dispersed in center regions (areas within about a 5 μm radius

from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a
5 density of 60 kg/m³ was as excellent as 215.5 cm.

Example 10

Modified resin beads were obtained in the same manner as in Example 2 except for the following. 50 parts by
10 weight of a styrene monomer was used, and after (first) polymerization at 135°C using 0.19 parts by weight of dicumyl peroxide as the initiator, the temperature of the reaction system was lowered to 125°C. 0.30 parts by weight of dicumyl peroxide as a polymerization initiator was dissolved in 350
15 parts by weight of a styrene monomer to prepare a second styrene monomer. The second styrene-based monomer was continuously dropped into the reaction solution of the first polymerization at a rate of 50 parts by weight per hour so that (second) polymerization of the second styrene monomer took
20 place while the resin beads were impregnated with the second styrene monomer. Then, expandable beads were obtained in the same manner as in example 7.

The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by
25 the TEM. The styrene resin particles with a particle diameter

of 0.03 μm to 0.3 μm were dispersed in surface regions (areas within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.08 μm to 0.4 μm were dispersed in center regions (areas within about a 5 μm radius
5 from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m^3 (amount of blowing agent: 14 parts by
10 weight) was as excellent as 155.5 cm. Furthermore, a molded article having a density of 30 kg/m^3 (amount of blowing agent: 16 parts by weight) was prepared in the same manner as in Example 1. The falling ball impact value measured of this molded article was as excellent as 120.5 cm.

15

Example 11

Modified resin beads were obtained in the same manner as in Example 10, and 14 parts by weight of pentane (n-pentane: isopentane = 80: 20, volume ratio) was added
20 instead of butane as the blowing agent. Then, the temperature inside the rotary mixer was raised to 30°C and kept for 6 hours. Then, the temperature was cooled to 25°C to obtain expandable beads.

The dispersion states of styrene resin in the obtained
25 modified resin beads and expandable beads were observed by

the TEM. The styrene resin particles with a particle diameter of 0.03 μm to 0.3 μm were dispersed in surface regions (areas within about 5 μm from the surfaces) and the styrene resin particles with a particle diameter of 0.08 μm to 0.4 μm were
5 dispersed in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a
10 density of 60 kg/m^3 (amount of blowing agent: 14 parts by weight) was as excellent as 155.5 cm. Furthermore, a molded article having a density of 30 kg/m^3 (amount of blowing agent: 16 parts by weight) was prepared in the same manner as in Example 1. The falling ball impact value measured of this
15 molded article was as excellent as 120.5 cm.

Comparative Example 1

Modified resin beads and expandable beads were obtained in the same manner as in Example 1 except that
20 trade name "TUF-2032" manufactured by Nippon Unicar Company Limited (crystallization peak temperature: 113°C, melt flow rate: 0.9 g/10 min., density: 0.923 g/cm^3 , molecular weight distribution (M_w/M_n): 4.5) was used as the linear low-density polyethylene-based resin (LLDPE) prepared by
25 using a Ziegler-Natta catalyst, the polymerization temperature

was 119°C and the amount of styrene monomer added was 185 parts by weight.

The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter of 0.05 μm to 0.15 μm were dispersed in surface regions (x12,800, areas within about 5 μm from the surfaces), but dispersion of the styrene resin particles was not observed and the styrene resin particles was the continuous phase in center regions (x12,800, areas within about a 5 μm radius from the centers). The cross-sectional pictures of the surface region and center region of the modified resin beads are shown in Fig. 6 and Fig. 7, respectively.

An expanded molded article was made in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a bulk density of 60 kg/m³ was 120.5 cm. This is significantly smaller than that of a molded article of the same density which contains polyethylene-based resin obtained using the metallocene compound as a catalyst.

Comparative Example 2

Modified resin beads and expandable beads were obtained in the same manner as in Example 1 except that the amount of styrene-based monomer used was 10 parts by

weight.

The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin in particulate form was hardly
5 observed in surface regions (areas within about 5 μm from the surfaces) and styrene resin in particulate form was not observed in center regions (areas within about a 5 μm radius from the centers) as well.

Next, the obtained expandable beads were immediately
10 fed to a pre-expanding machine and steam was introduced at a pressure of 0.02 MPa to pre-expand the beads. The beads, however, hardly expanded and pre-expanded beads that can be adapted for expansion molding could not be obtained.

15 Comparative Example 3

Resin beads were obtained in the same manner as in Example 1 except that the amount of the initiator used was 1.0 parts by weight. The obtained resin beads contained a large amount of fine powder other than the modified resin beads.
20 The fine powder was styrene resin powder and it was generated due to the styrene monomer being polymerized before the impregnation of the inside of the resin beads with the monomer. For this reason, the polyethylene-based resin could not be modified with a desired amount of the styrene resin.

25 An expanded molded article for the evaluation of

physical properties could not be obtained since the fine particles hindered the fusion of the expanded beads at the expansion molding.

5 Comparative Example 4

Modified resin beads and expandable beads were obtained in the same manner as in Example 1 except that benzoyl peroxide was used as the initiator and the polymerization temperature was 90°C.

10 The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter greater than 1 μm were dispersed in surface regions (areas within 5 μm from the surface). A part of the styrene resin was
15 in a continuous state in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a
20 density of 60 kg/m^3 was as poor as 95.5 cm.

Comparative Example 5

Modified resin beads were obtained in the same manner as in Example 7 except that benzoyl peroxide was used
25 as the initiator and the polymerization temperature was 90°C

in the first polymerization and dicumyl peroxide was used as the initiator and the polymerization temperature was 130°C in the second polymerization. Then, expandable beads were obtained in the same manner as in Example 1.

5 The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter greater than 1 μm were dispersed in surface regions (areas within 5 μm from the surfaces) and center regions (areas
10 within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m^3 was as poor as 120.5 cm.

15

Comparative Example 6

Modified resin beads were obtained in the same manner as in Example 7 except that dicumyl peroxide was used as the initiator and the polymerization temperature was
20 130°C in the first polymerization and benzoyl peroxide was used as the initiator and the polymerization temperature was 90°C in the second polymerization. Then, expandable beads were obtained in the same manner as in Example 1.

The dispersion states of styrene resin in the obtained
25 modified resin beads and expandable beads were observed by

the TEM. The styrene resin particles with a particle diameter greater than 1 μm were dispersed in surface regions (areas within 5 μm from the surfaces). The styrene resin was in a continuous state in center regions (areas within about a 5 μm radius from the centers).

Next, an expanded molded article was obtained in the same manner as in Example 1, and the falling ball impact value was measured. The value of the molded article having a density of 60 kg/m^3 was as poor as 100.5 cm.

10

Comparative Example 7

Modified resin beads were obtained in the same manner as in Example 2 except that the amount of the second styrene monomer was 834 parts by weight and it was dropped continuously into the reaction solution of the first polymerization over 10 hours. Then, expandable beads were obtained in the same manner as in Example 1.

The dispersion states of styrene resin in the obtained modified resin beads and expandable beads were observed by the TEM. The styrene resin particles with a particle diameter of 0.07 μm to 0.4 μm were dispersed in surface regions (x19,300, areas within about 5 μm from the surfaces), but in center regions (x19,300, areas within about a 5 μm radius from the centers) the particulate styrene resin formed a continuous phase and as a result, the styrene resin particles

25

had a particle diameter greater than 0.8 μm . The cross-sectional pictures of the surface region and the center region are shown in Fig. 8 and Fig. 9, respectively.

Next, an expanded molded article having a density of
5 60 kg/m^3 was made in the same manner as in Example 1, and the falling ball impact value was measured. It was as poor as 120.5 cm.

The conditions for making the modified resin beads, the blowing agent used, the bulk density of the pre-expanded
10 beads and the falling ball impact value of the expanded molded article according to Examples 1-11 and Comparative Examples 1-7 are shown in Table 1 and Table 2.

TABLE 1

	Examples										
	1	2	3	4	5	6	7	8	9	10	11
Condi- tions	PE Resin (pbw)	FMRN-063 100	Evolve- F201 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100
	Coloring Agent (pbw)			iron oxide 25	CB 3						
	Crz. Peak Temp. (°C)	101	108	101	101	101	101	101	101	101	101
	Inorg. Nucleating Agent (pbw)	talc 0.5	talc 0.5	talc 0.5	talc 0.5	talc 0.5	Talc 0.5	silica 0.5	talc 0.5	talc 0.5	talc 0.5
	1 st . Styrene-based Monomer (pbw)	SM 66	SM 66	SM 66	SM 66	SM ⁺ α -MSM 95+5	SM 50	SM 50	SM 120	SM 50	SM 50
	2 nd . Styrene-based monomer (pbw)	SM 534	SM 534	SM 534	SM 534		SM 350	SM 350	SM 80	SM 350	SM 350
	1 st . Polym. Temp. (°C)	130	130	130	130	130	115	140	130	135	135
	2 nd . Polym. Temp. (°C)		130	130	130		115	140	130	125	125
	(1 st .) Polym. Initiator Amt. (pbw)	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
	(2 nd .) Polym. Initiator Amt. (pbw)		0.30	0.30	0.30		0.30	0.30	0.30	0.30	0.30
	Blowing Agent	butane 60	butane 60	butane 60	butane 60	butane 60	butane 60	butane 60	butane 60	butane 60	butane 60
Bulk Density (kg/cm ³)		150	60	30							
		250.5	260.5	175.5	105.5	155.5	125.5	155.5	215.5	155.5	155.5
Falling Ball Impact Value (cm)						245.5	120.5	160.5	120.5	120.5	120.5

pbw: parts by weight crz: crystallization

TABLE 2

	Comparative, Examples						
	1	2	3	4	5	6	7
PE Resin (pbw)	TUF-2032 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100	FMRN-063 100
Crz. Peak Temp. (°C)	113	101	101	101	101	101	101
Inor. Nucleating Agent (pbw)	talc 0.5	Talc 0.5	Talc 0.5	talc 0.5	talc 0.5	talc 0.5	talc 0.5
1 st . Styrene-based monomer (pbw)	SM 185	SM 10	SM 100	SM 100	SM 50	SM 50	SM 66
2 nd . Styrene-based monomer (pbw)					SM 350	SM 350	SM 834
1 st . Polym. Temp. (°C)	119	130	130	90	90	130	130
2 nd . Polym. Temp. (°C)					130	90	130
(1 st .) Polym. Initiator (pbw)	0.19	0.19	1.0	0.19	0.19	0.19	0.19
(2 nd .) Polym. Initiator (pbw)					0.30	0.30	0.30
Blowing Agent	butane	butane	butane	butane	butane	butane	butane
Bulk Density(kg/cm ³)	60			60	60	60	60
Falling Ball Impact Value (cm)	120.5			95.5	120.5	100.5	120.5

pbw: parts by weight crz: crystallization

In Tables 1 and 2, PE refers to polyethylene-based resin, SM refers to a styrene monomer and α -MSM refers to an α -methylstyrene monomer.

5 The invention thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

10 Furthermore, the present invention is related to Japanese Patent Application No. 2004-258792 filed on September 6, 2004, whose priority is claimed and the disclosure of which is incorporated by reference in its entirety.

15

[Name of the Document] Claims

[Claim 1] A method for producing styrene-modified linear low-density polyethylene-based resin beads, comprising the
5 steps of:

dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and contain an inorganic nucleating agent, 50 to 800 parts by
10 weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into an aqueous suspension containing a dispersant;

impregnating the polyethylene-based resin beads with
15 the styrene-based monomer under heating the resulting dispersion at such a temperature that the styrene-based monomer does not substantially polymerize; and

performing polymerization of the styrene-based monomer at a temperature of $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$
20 is a crystallization peak temperature of the polyethylene-based resin beads).

[Claim 2] A method for producing styrene-modified linear low-density polyethylene-based resin beads according to Claim
25 1, wherein the styrene-based monomer is used in an amount of

50 to 300 parts by weight.

[Claim 3] A method for producing styrene-modified linear low-density polyethylene-based resin beads according to claim
5 1, wherein the low-density polyethylene-based resin beads have a molecular weight distribution (M_w/M_n) of 1.5 to 3.5 measured by GPC and a density of 0.910 to 0.925 g/cm³.

[Claim 4] A method for producing styrene-modified linear
10 low-density polyethylene-based resin beads, comprising the steps of:

dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and
15 contain an inorganic nucleating agent, 30 to 300 parts by weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into an aqueous suspension containing a dispersant;

20 impregnating the polyethylene-based resin beads with the styrene-based monomer under heating the resulting dispersion at such a temperature that the styrene-based monomer does not substantially polymerize;

performing first polymerization of the styrene-based
25 monomer at a temperature of $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$

is a crystallization peak temperature of the polyethylene-based resin beads); and

subsequent to the first polymerization, adding a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer and adjusting the temperature of the resulting dispersion to $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a crystallization peak temperature of the polyethylene-based resin beads), so that impregnation of the low-density polyethylene-based resin beads with the styrene-based monomer and second polymerization take place, wherein the total amount of the styrene-based monomers used in the first and second polymerization is 50 to 800 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads.

15

[Claim 5] A method for producing styrene-modified linear low-density polyethylene-based resin beads according to claim 4, wherein the low-density polyethylene-based resin beads have a molecular weight distribution (M_w/M_n) of 1.5 to 3.5 measured by GPC and a density of 0.910 to 0.925 g/cm³.

20

[Claim 6] A method for producing styrene-modified linear low-density polyethylene-based expandable resin beads, comprising the steps of:

25

dispersing 100 parts by weight of non-crosslinked

linear low-density polyethylene-based resin beads which are
polymerized using a metallocene compound as a catalyst and
contain an inorganic nucleating agent, 50 to 800 parts by
weight of a styrene-based monomer and 0.1 to 0.9 parts by
5 weight of a polymerization initiator relative to 100 parts by
weight of the styrene-based monomer into an aqueous
suspension containing a dispersant;

impregnating the polyethylene-based resin beads with
the styrene-based monomer under heating the resulting
10 dispersion at such a temperature that the styrene-based
monomer does not substantially polymerize;

performing polymerization of the styrene-based
monomer at a temperature of $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$
is a crystallization peak temperature of the polyethylene-based
15 resin beads); and

impregnating the resin beads during or after the
polymerization with a volatile blowing agent.

[Claim 7] A method for producing styrene-modified linear
20 low-density polyethylene-based expandable resin beads
according to claim 6, wherein the styrene-based monomer is
used in an amount of 50 to 300 parts by weight.

[Claim 8] A method for producing styrene-modified linear
25 low-density polyethylene-based expandable resin beads

according to claim 6, wherein the low-density polyethylene-based resin beads have a molecular weight distribution (Mw/Mn) of 1.5 to 3.5 measured by GPC and a density of 0.910 to 0.925 g/cm³.

5

[Claim 9] A method for producing styrene-modified linear low-density polyethylene-based expandable resin beads, comprising the steps of:

dispersing 100 parts by weight of non-crosslinked
10 linear low-density polyethylene-based resin beads which are polymerized using a metallocene compound as a catalyst and contain an inorganic nucleating agent, 30 to 300 parts by weight of a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by
15 weight of the styrene-based monomer into an aqueous suspension containing a dispersant;

impregnating the polyethylene-based resin beads with the styrene-based monomer under heating the resulting dispersion at such a temperature that the styrene-based
20 monomer does not substantially polymerize;

performing first polymerization of the styrene-based monomer at a temperature of (T + 10) to (T + 35)°C (where T°C is a crystallization peak temperature of the polyethylene-based resin beads);

25 subsequent to the first polymerization, adding a

styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer and adjusting the temperature of the resulting dispersion to $(T + 10)$ to $(T + 35)^{\circ}\text{C}$ (where $T^{\circ}\text{C}$ is a
5 crystallization peak temperature of the polyethylene-based resin beads), so that impregnation of the polyethylene-based resin beads with the styrene-based monomer and second polymerization take place, wherein the total amount of the styrene-based monomers used in the first and second
10 polymerization is 50 to 800 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads; and
impregnating the resin beads during or after the polymerization with a volatile blowing agent.

15 [Claim 10] A method for producing styrene-modified linear low-density polyethylene-based expandable resin beads according to claim 9, wherein the low-density polyethylene-based resin beads have a molecular weight distribution (M_w/M_n) of 1.5 to 3.5 measured by GPC and a
20 density of 0.910 to 0.925 g/cm^3 .

[Claim 11] Styrene-modified linear low-density polyethylene-based resin beads, comprising 50 to 800 parts by weight of styrene-based resin relative to 100 parts by weight of
25 non-crosslinked linear low-density polyethylene-based resin

which is polymerized using a metallocene compound as a catalyst, wherein styrene-based resin is dispersed a form particles in a beads, and the particle diameter is 0.8 μm or smaller in a surface region within at least 5 μm from the bead surface and a center region within a 5 μm radius from the bead center.

[Claim 12] Styrene-modified linear low-density polyethylene-based expandable resin beads, comprising a volatile blowing agent and 50 to 800 parts by weight of styrene-based resin relative to 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin which is polymerized using a metallocene compound as a catalyst, wherein styrene-based resin is dispersed a form particles in a beads, and the particle diameter is 0.8 μm or smaller in a surface region within at least 5 μm from the bead surface and a center region within a 5 μm radius from the bead center.

[Claim 13] Pre-expanded beads having a bulk density of 10 to 300 kg/m^3 obtained by pre-expanding the styrene-modified linear low-density polyethylene-based expandable resin beads of claim 12.

[Claim 14] An expanded molded article having a density of 10

to 300 kg/m³ obtained by expansion molding of the pre-expanded beads of claim 13.