

DESCRIPTION

TITLE

STYRENIC COPOLYMER AND PRODUCTION METHOD THEREFOR, AND
EXTRUDED FOAM SHEET AND MOLDED ARTICLE THEREOF

FIELD

[0001]

The present invention relates to a styrenic copolymer and to a production method for the same, and to an extruded foam sheet and to a molded article of the same.

BACKGROUND

[0002]

Styrene-based resins have excellent transparency and formability, and are therefore widely used as molding materials for household appliances, office machinery, sundry goods and housing equipment, as well as food packaging materials. With greater requirements for decreasing thicknesses, lower weights and diversifying shapes of products in recent years, there is a demand for styrene-based resins with satisfactory outer appearance and excellent formability. Methods of adding ultrahigh molecular weight components to styrene-based resins are known to be effective as methods for improving the formability of styrene-based resins into extruded sheets and the like.

[0003]

As one such method, PTL 1 describes a styrenic copolymer for highly-branched foaming, containing a highly-branched ultrahigh molecular weight copolymer obtained by polymerization of a monovinyl compound with styrene as an essential component, and a solvent-soluble polyfunctional vinyl copolymer having an average of two or more vinyl groups in the molecule and having a branched structure. The styrene-based resin composition for highly-branched foaming is disclosed as having an excellent balance between melt tension and melt extensibility, and being able to reduce gelatinous material in the strands extruded from the porous die of the polymerizer. In PTL 2, for measurement of the uniaxial extensional viscosity of a polystyrenic copolymer under prescribed conditions, the description focuses on the ratio between the slope of a first-order approximation line in the nonlinear region of a logarithmic plot of a time-extensional viscosity curve, and the slope of a first-order approximation line in the linear region of the curve. Specifically, it is stated that a container with lower weight can be obtained without reducing its physical properties if the ratio is in the range of 2.0 to 6.0.

[CITATION LIST]

[PATENT LITERATURE]

[0004]

[PTL 1] Japanese Unexamined Patent Publication No. 2013-100427

5 [PTL 2] Japanese Unexamined Patent Publication No. 2014-189764

SUMMARY

[TECHNICAL PROBLEM]

[0005]

10 It has been found, however, that the reduction in gelatinous material in the highly-
branched foaming styrenic copolymer of PTL 1 is not sufficient, and therefore room for further
improvement exists. With PTL 2, although the range is specified for the ratio between the slope
of a first-order approximation line in the nonlinear region of a logarithmic plot of the time-
extensional viscosity curve, and the slope of a first-order approximation line in the linear region
15 of the curve, when the uniaxial extensional viscosity of a polystyrenic copolymer is measured
under prescribed conditions, it has been found that the reduction in gelatinous substance is still
insufficient, and therefore room for further improvement exists.

The present invention has been devised in light of these circumstances of the prior art,
and its object is to provide a styrenic copolymer with excellent formability and low gelatinous
20 material, and a production method for the same.

[SOLUTION TO PROBLEM]

[0006]

25 The present inventors have carried out diligent research with the aim of achieving this
object, and as a result we have completed this invention upon finding that a styrenic copolymer
with excellent formability and low gelatinous material can be obtained by composing a styrenic
copolymer using a prescribed conjugated divinyl compound and a prescribed monovinyl
compound in a suitable content ratio, and controlling the molecular weight and molecular weight
distribution of the styrenic copolymer to within a suitable range.

30 Specifically, the present invention is as follows.

[1]

A styrenic copolymer of a conjugated divinyl compound having a number-average
molecular weight (Mn) of 850 to 100,000 and at least one monovinyl compound comprising at
least a styrenic compound, wherein

35 the content of the conjugated divinyl compound is 2.0×10^{-6} to 4.0×10^{-4} mol, per mole
of the monovinyl compound,

the styrenic copolymer has a weight-average molecular weight (M_w) of 200,000 to 500,000, and

the proportion having a molecular weight of 2,000,000 or greater is 0.3% to 6.0%.

[2]

5 The styrenic copolymer according to [1] above, wherein the number-average molecular weight (M_n) of the conjugated divinyl compound is 1,000 to 30,000.

[3]

The styrenic copolymer according to [1] or [2] above, wherein the conjugated divinyl compound has a chain structure.

10 [4]

The styrenic copolymer according to any one of [1] to [3] above, wherein conjugated vinyl groups of the conjugated divinyl compound are located at the ends thereof.

[5]

15 The styrenic copolymer according to any one of [1] to [4] above, wherein the ratio of the Z-average molecular weight (M_z) with respect to the M_w of the styrenic copolymer is 1.8 to 5.0.

[6]

The styrenic copolymer according to any one of [1] to [5] above, wherein the proportion of the styrenic copolymer having a molecular weight of 1,000,000 or greater is 4.0% to 20.0%.

[7]

20 The styrenic copolymer according to any one of [1] to [6] above, wherein the initial rise strain is 0.2 to 1.3, and the maximum rise ratio is 1.2 to 5.0.

[8]

The styrenic copolymer according to any one of [1] to [7] above, wherein the conjugated divinyl compound is (hydrogenated) polybutadiene di(meth)acrylate.

25 [9]

The styrenic copolymer according to any one of [1] to [8] above, wherein the total content of styrenic compound dimers and trimers is from 0.01 to 0.30 wt% with respect to 100 wt% of the styrenic copolymer.

[10]

30 A production method for a styrenic copolymer, which includes polymerizing the styrenic copolymer according to any one of [1] to [9] above using continuous solution polymerization or continuous bulk polymerization.

[11]

35 An extruded foam sheet comprising the styrenic copolymer according to any one of [1] to [9] above and having a thickness of 0.5 mm to 5.0 mm.

[12]

A secondary molded article produced by using the extruded foam sheet according to [11] above.

[ADVANTAGEOUS EFFECTS OF INVENTION]

5 **[0007]**

According to the present invention it is possible to provide a styrenic copolymer with excellent formability and low gelatinous material, and a production method for the same.

BRIEF DESCRIPTION OF DRAWINGS

10 **[0008]**

FIG. 1 is a double logarithmic graph plotting Hencky strain on the abscissa and extensional viscosity on the ordinate, for the styrenic copolymers obtained in the Examples and Comparative Examples.

15 **DESCRIPTION OF EMBODIMENTS**

[0009]

An embodiment of the invention (hereunder referred to as “this embodiment”) will now be explained as an example, with the understanding that the invention is not limited to this embodiment.

20 **[0010]**

<Styrenic copolymer>

The styrenic copolymer of this embodiment is a styrenic copolymer of a conjugated divinyl compound having a number-average molecular weight (Mn) of 850 to 100,000 and at least one monovinyl compound comprising at least a styrenic compound, wherein the content of the conjugated divinyl compound is 2.0×10^{-6} to 4.0×10^{-4} mol, per mole of the monovinyl compound. The styrenic copolymer also has a weight-average molecular weight (Mw) of 200,000 to 500,000, and its proportion of molecular weight of 2,000,000 or greater is 0.3% to 6.0%.

[0011]

30 According to this embodiment, it is possible to provide a styrenic copolymer with excellent formability and low gelatinous material. Specifically, while not being limited to theory, presumably the molecular chains of the obtained styrenic copolymer of this embodiment can be easily formed by a plurality of molecular chain portions composed mainly of a monovinyl compound and conjugated divinyl compound-derived portions mutually linked between the molecular chain portions, while the interval between the molecular chain portions can be
35 restricted to a prescribed distance (it is thought to be easier to form H-shaped branched portions

in the molecular chain of the styrenic copolymer). By forming the styrenic copolymer in this manner, each of the molecular chains of the styrenic copolymer can be more effectively entangled together (this effect being referred to as an “entanglement effect”), thus allowing the formability of the styrenic copolymer to be improved. At the same time, since the conjugated divinyl compound content and the molecular weight and molecular weight distribution of the styrenic copolymer are limited to prescribed ranges for this embodiment, it is possible to effectively improve the formability of the styrenic copolymer while effectively preventing gelling of the styrenic copolymer. According to this embodiment, therefore, it is possible to provide a styrenic copolymer with excellent formability and low gelatinous material, and the low gelatinous material allows a satisfactory molded outer appearance to be obtained from the styrenic copolymer.

[0012]

<Monovinyl compound >

The styrenic copolymer of this embodiment contains at least one monovinyl compound comprising at least a styrenic compound (as the monomer that is to form the styrenic copolymer), and the monovinyl compound may consist of a styrenic compound (monomer) alone, or it may consist of a mixture having, in addition to the styrenic compound, another monovinyl group that is copolymerizable with the styrenic compound. In addition to styrenic compounds, the monovinyl compound is not particularly restricted so long as it is copolymerizable with the styrenic compound, and examples include vinyl-based compounds such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, cetyl (meth)acrylate and (meth)acrylonitrile, and dimethyl maleate, dimethyl fumarate, diethyl fumarate, ethyl fumarate, maleic anhydride, maleimide and nucleosubstituted maleimides. Examples of styrenic compounds include styrene, α -methylstyrene, paramethylstyrene, ethylstyrene, propylstyrene, butylstyrene, chlorostyrene and bromostyrene, with styrene being preferred. The content of the styrenic compound is preferably 50 mol% or greater, more preferably 70 mol% or greater and even more preferably 90 mol% or greater, of the monovinyl compound content.

[0013]

<Conjugated divinyl compound >

The conjugated divinyl compound for this embodiment is a compound having a number-average molecular weight (M_n) of 850 to 100,000, and having two or more conjugated vinyl groups in the molecule. The conjugated divinyl compound of this embodiment has preferably a chain structure instead of a reticulate structure, and it may either have or not have side chains on the main chain. If it has a chain structure, it will be possible to form a more linear molecular chain, thus tending to help increase the entanglement effect. The side chains preferably have no more than 6 carbon atoms and preferably no more than 4 carbon atoms.

The conjugated vinyl groups in the conjugated divinyl compound may be located at any position in the molecule, and preferably two conjugated vinyl groups of the two or more conjugated vinyl groups are located at different ends in the molecule. When the conjugated divinyl compound has a chain structure, the two conjugated vinyl groups are more preferably located at different ends of the main chain (that is, more preferably both ends of the main chain are conjugated divinyl groups). Having the conjugated vinyl groups located at the ends can increase the polymerization reactivity.

Moreover, when the conjugated divinyl compound has a chain structure and 3 or more conjugated vinyl groups are present, preferably two conjugated vinyl groups of the 3 or more conjugated vinyl groups are located at the ends, and more preferably the remaining one or more conjugated vinyl groups are also located at the ends.

Incidentally, when a large number of conjugated vinyl groups are present in the conjugated divinyl compound, the number of bifurcation points increases and gelation may be more likely to occur in the reactor or during the process of collecting the starting materials, or the transparency of the styrenic copolymer may be impaired, so that it may be necessary to wash the reactor, thus lowering productivity, and therefore the number is preferably no greater than 5, more preferably no greater than 4 and even more preferably no greater than 3. From the same viewpoint, the number of conjugated vinyl groups in the conjugated divinyl compound is most preferably two.

The “ends” referred to here may be located at the furthestmost ends of the molecular chain, but as long as the conjugated vinyl groups are present near the ends they will have effective reactivity with the monovinyl compound and gelation can be minimized, and therefore for the purpose of this embodiment, the “ends” may be portions within a certain range of the molecular chain that includes the locations (atoms) at the furthestmost ends of the molecular chain (end portions) (or in other words, the conjugated vinyl groups may be located near the ends). The portions that are within such a range are not limited, but they are preferably no more than 20%, more preferably no more than 15%, even more preferably no more than 10% and most preferably no more than 5% of the extended chain length of the conjugated divinyl compound.

[0014]

For this embodiment, a conjugated vinyl group is a group having an olefinic double bond that is copolymerizable with a monovinyl compound, and a structure that forms a conjugated system with the olefinic double bond (examples including but not limited to carbonyl groups and aryl groups). The conjugated vinyl group is not particularly restricted and may be, for example, an aryl group substituted with an acryloyl group or a vinyl group, and the structure in the conjugated divinyl compound having a conjugated vinyl group is not particularly restricted and may be, for example, a structure with addition of (meth)acrylate, urethane (meth)acrylate,

aromatic vinyl, maleic acid or fumaric acid. Incidentally, the two or more conjugated vinyl groups may be the same or different.

[0015]

The number-average molecular weight (M_n) of the conjugated divinyl compounds for this embodiment is 850 to 100,000, preferably 1,000 to 100,000, more preferably 1,000 to 80,000, even more preferably 1200 to 80,000, yet more preferably 1500 to 60,000 and most preferably 1500 to 30,000. If the number-average molecular weight (M_n) is less than 850, the distance between the conjugated vinyl groups in the conjugated divinyl compound will be short, thereby shortening the distance between the polymer chains bonded to the conjugated divinyl compound, making a sufficient entanglement effect impossible, and resulting in inferior formability. If the molecular weight is greater than 100,000, an undesirable situation is created because the distance between the conjugated vinyl groups of the conjugated divinyl compound will be long, thereby lowering the reactivity of the conjugated vinyl groups at the ends (the large molecular weight of the conjugated divinyl compound reduces reaction of the terminal conjugated vinyl groups), and lowering the amount of high-molecular-weight components produced. The number-average molecular weight (M_n) of the conjugated divinyl compound is the number-average molecular weight (M_n) in terms of polystyrene, as measured by gel permeation chromatography (GPC).

[0016]

The main chain structure of the conjugated divinyl compound for this embodiment is not particularly restricted, and may be a polyolefin such as polyethylene, polypropylene or polyisoprene, or polystyrene, polybutadiene, hydrogenated polybutadiene, polyphenylene ether, polyester or polyphenylene sulfide, for example.

[0017]

Specific conjugated divinyl compounds include terminal di(meth)acrylate compounds such as (hydrogenated) polybutadiene-terminal (meth)acrylate (the term “(hydrogenated)” indicating that the compound may be either hydrogenated or non-hydrogenated, same hereunder), polyethylene glycol-terminal (meth)acrylate, polypropylene glycol-terminal (meth)acrylate, ethoxylated bisphenol A-terminal (meth)acrylate and ethoxylated bisphenol F-terminal (meth)acrylate, and terminal urethane acrylate compounds such as (hydrogenated) polybutadiene-terminal urethane acrylate, polyethylene glycol-terminal urethane acrylate, polypropylene glycol-terminal urethane acrylate, ethoxylated bisphenol A-terminal urethane acrylate and ethoxylated bisphenol F-terminal urethane acrylate. In the case of polypropylene glycol-terminal (meth)acrylate, for example, the number of propylene glycol bonds of the repeating unit is determined so that the number-average molecular weight (M_n) is 850 to 100,000. From the viewpoint of compatibility with the styrenic copolymer, the conjugated

divinyl compound is preferably a (hydrogenated) polybutadiene-terminal (meth)acrylate, polystyrene-terminal (meth)acrylate or polyphenylene ether-terminal divinyl compound. The terms “terminal” or “both ends” in the compound names means that the conjugated vinyl group is located at both of the furthestmost ends.

5 **[0018]**

<Conjugated divinyl compound content>

The conjugated divinyl compound content for this embodiment is 2.0×10^{-6} to 4.0×10^{-4} mol, preferably 5.0×10^{-6} to 3.5×10^{-4} mol, more preferably 1.5×10^{-5} to 3.0×10^{-4} mol and even more preferably 2.0×10^{-5} to 2.5×10^{-4} mol, per mole of the monovinyl compound. If the
10 content is less than 2.0×10^{-6} mol, it will be difficult to produce sufficient entanglement between the polymers and strain hardening either will not be exhibited, or the degree of strain hardening will be minimal, and therefore the wall thickness of the molded article will fail to be uniform, the molded article may undergo tearing during molding, and the formability will be inferior. If the content is greater than 4.0×10^{-4} mol, on the other hand, more gelatinous material will be
15 generated and the outer appearance of the molded article will be poor.

[0019]

<Molecular weight>

The weight-average molecular weight (Mw) of the styrenic copolymer for this embodiment is 200,000 to 500,000, preferably 220,000 to 480,000 and more preferably 240,000
20 to 450,000. If the Mw of the styrenic copolymer is 200,000 to 500,000, the strength of the styrenic copolymer will be ensured and generation of gelatinous material will be minimized, thereby allowing the formability and flow property to be further improved. The ratio of the Z-average molecular weight (Mz) with respect to the weight-average molecular weight (Mw) of the styrenic copolymer of this embodiment is preferably 1.8 to 5.0, more preferably 2.0 to 4.8 and
25 even more preferably 2.1 to 4.7. If the ratio of the Mz to Mw of the styrenic copolymer is in the range of 1.8 to 5.0, the strength of the styrenic copolymer will be ensured and generation of gelatinous material will be minimized, thereby allowing the formability and flow property to be further improved.

In the styrenic copolymer of this embodiment, incidentally, the weight-average molecular
30 weight (Mw) and the ratio of the Z-average molecular weight (Mz) with respect to the weight-average molecular weight (Mw) can be controlled by the type and addition amount of the conjugated divinyl compound, the reaction temperature, the residence time, the type and addition amount of the polymerization initiator, the type and amount of the solvent, and the type and addition amount of the chain transfer agent, during radical polymerization of the styrene-based
35 monomer. Specifically, control of the weight-average molecular weight (Mw) may include, but is not limited to, for example, increasing the amount of polymerization initiator added for

polymerization, lowering the reaction temperature for polymerization, reducing the amount of polymerization solvent used, and lengthening the residence time for polymerization, during the method of production, as this will allow the desired shape of the molecular chain to be formed and can increase the high-molecular-weight component portion to a suitable degree in the styrenic copolymer that is obtained.

The weight-average molecular weight (M_w), Z-average molecular weight (M_z), and the proportions of molecular weight of 1,000,000 or greater and of 2,000,000 or greater (described below) in the styrenic copolymer are the weight proportions in the differential molecular weight distribution as measured by gel permeation chromatography (GPC).

[0020]

<Proportion of high-molecular-weight component>

The proportion of molecular weight of 2,000,000 or greater in the styrenic copolymer of this embodiment is 0.3 to 6.0%, preferably 0.8 to 5.0% and more preferably 1.4 to 4.8%. If the proportion of molecular weight of 2,000,000 or greater is in the range of 0.3 to 6.0%, the content of the gelatinous material can be reduced to an extreme degree. The proportion of molecular weight 1,000,000 or greater is preferably 4.0 to 20.0%, more preferably 5.0 to 18.0% and even more preferably 5.0 to 15.0%. If the proportion of molecular weight 1,000,000 or greater is in the range of 4.0 to 20.0%, it will be possible to obtain a styrenic copolymer with excellent formability and flow properties.

The molecular weight proportion of the styrenic copolymer of this embodiment can be controlled by the type and addition amount of the conjugated divinyl compound, the reaction temperature, the residence time, the type and addition amount of the polymerization initiator, the type and amount of the solvent, and the type and addition amount of the chain transfer agent, during radical polymerization of the styrene-based monomer. Specifically, control of the proportion of molecular weight of 2,000,000 or greater and of molecular weight 1,000,000 or greater may include, but is not limited to, for example, increasing the amount of polymerization initiator added for polymerization, lowering the reaction temperature for polymerization, reducing the amount of polymerization solvent used, and lengthening the residence time for polymerization, during the method of production, as this will allow the low-molecular-weight component portion to be reduced and will allow the high-molecular-weight component portion to be increased while obtaining a suitable proportion of molecular weight of 2,000,000 or greater and of molecular weight 1,000,000 or greater, in the styrenic copolymer that is obtained.

[0021]

<Melt mass-flow rate (MFR)>

The melt mass-flow rate (MFR) of the styrenic copolymer of this embodiment is preferably 0.5 to 5.0. It is more preferably 0.6 to 4.0, even more preferably 0.7 to 3.5 and most

preferably 0.8 to 3.0. If the melt mass-flow rate is in the range of 0.5 to 5.0, a styrenic copolymer with a more excellent balance between formability and flow properties will be obtained.

[0022]

<Initial rise strain, maximum rise strain and maximum rise ratio>

5 The initial rise strain of the styrenic copolymer of this embodiment is preferably 0.2 to 1.3, more preferably 0.3 to 1.1 and even more preferably 0.4 to 1.0. For the purpose of the present specification, “initial rise strain” refers to the strain exhibited with strain hardening, and it is an index of the formability. A smaller initial rise strain, i.e. more rapid rise, results in more strain hardening from the low-stretched state, and more excellent formability, so that the wall
10 thickness of the molded article may be more uniform and the molded article may be reduced in thickness.

[0023]

 The maximum rise ratio of the styrenic copolymer of this embodiment is preferably 1.2 to 5.0, more preferably 1.3 to 4.8 and even more preferably 1.4 to 4.6. Throughout the present
15 specification, “maximum rise ratio” means (extensional viscosity in the nonlinear region of the maximum rise strain/extensional viscosity in the linear region of the maximum rise strain), and “maximum rise strain” means the Hencky strain at which the extensional viscosity is maximal. The maximum rise ratio is an index representing the degree of strain hardening for the maximum rise strain. A larger maximum rise ratio corresponds to a greater degree of strain hardening, and
20 more excellent formability. If the maximum rise ratio is 1.2 or greater, then the extensional viscosity will increase during high strain, i.e. when the resin is stretched thinly during the molding process, tending to result in uniform wall thickness of the molded article and lower likelihood for it to tear during molding. If the maximum rise ratio is 5.0 or lower, the extensional viscosity during molding will not be too high, as is preferred from the viewpoint of balance
25 between productivity and moldability.

[0024]

<Total content of styrenic compound dimers and trimers>

 The total content of styrenic compound dimers and trimers (compounds with two or three molecules bonded together) in the styrenic copolymer of this embodiment is preferably 0.01 to 0.30 wt%, more preferably 0.01 to 0.25 wt% and even more preferably 0.02 to 0.20 wt%, with
30 respect to 100 wt% of the styrenic copolymer. If the total content of styrenic compound dimers and trimers is 0.01 to 0.30 wt%, less gummy residue will form during secondary molding, the yield of molded articles with satisfactory outer appearance may be increased, and the odor of the molded article may be reduced. If the total content of styrenic compound dimers and trimers is
35 greater than 0.30 wt%, liquid drip marks may form on the molded article and the outer appearance may be poor.

[0025]

<Additives>

The styrenic copolymer of this embodiment may, if necessary, contain a rubber-reinforced aromatic vinyl-based resin such as HI-PS resin or MBS resin, or an aromatic vinyl-based thermoplastic elastomer such as SBS, as a rubber-containing component, in an amount of about 1% to 50%. In order to minimize thermal decomposition of the polymer during the step of recovering the unreacted monomer, a process stabilizer such as 2-[1-(2-hydroxy-3,5-di-t-phenylpentyl)ethyl]-4,6-di-t-phenylpentyl acrylate may also be included. A higher fatty acid or its salt such as stearic acid, zinc stearate, calcium stearate or magnesium stearate, a lubricant such as ethylene bisstearylamine, a plasticizer such as liquid paraffin, or an antioxidant may also be included. In addition, additives commonly used in the field of styrene-based resins, such as nucleating agents, flame retardants and coloring agents may also be added in combination to the styrenic copolymer, in ranges that do not interfere with the object of this embodiment. The additives are not particularly restricted, and for example, nucleating agents such as talc, flame retardants such as hexabromocyclododecane and coloring agents such as titanium oxide and carbon black may be mentioned. The styrene-based resin may be used as pellets, and ethylene bisstearylamine, zinc stearate, magnesium stearate or the like may be used to cover the pellets as an external lubricant for the pellets.

[0026]

Antioxidants are components that generally stabilize peroxide radicals such as hydroperoxy radicals generated during hot molding or light exposure, or decompose generated peroxides such as hydroperoxide. The antioxidant is not particularly restricted, and for example, it may be a hindered phenol-based antioxidant, peroxide decomposer or the like. A hindered phenol-based antioxidant acts as a radical chain inhibitor, and a peroxide decomposer further decomposes peroxides generated in the system to stable alcohols, preventing autooxidation. Hindered phenol-based antioxidants include, but are not limited to, 2,6-di-t-butyl-4-methylphenol, styrenated phenol, n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2-t-butyl-6-(3-t-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, 2-[1-(2-hydroxy-3,5-di-t-pentylphenyl)ethyl]-4,6-di-t-pentylphenyl acrylate, 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), alkylated bisphenols, tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane and 3,9-bis[2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)-propionyloxy]-1,1-dimethylethyl]-2,4,8,10-tetraoxyspiro[5.5]undecane. Peroxide decomposers include, but are not limited to, organic phosphorus-based peroxide decomposers such as trisnonylphenyl phosphite, triphenyl phosphite and tris(2,4-di-t-butylphenyl)phosphite, and organic sulfur-based peroxide decomposers such as dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-

3,3'-thiodipropionate, pentaerythrityltetrakis(3-lauryl thiopropionate), ditridecyl-3,3'-thiodipropionate and 2-mercaptobenzimidazole. The amount of antioxidant added is preferably 0.01 part by weight to 1 part by weight and more preferably 0.1 part by weight to 0.5 part by weight, with respect to 100 parts by weight of the styrenic copolymer in the extruded foam sheet.

[0027]

Examples of flame retardants include, but are not limited to, bromine-based flame retardants such as hexabromocyclododecane, brominated SBS block copolymer and 2,2-bis(4'(2",3"-dibromoalkoxy)-3',5'-dibromophenyl)-propane, and brominated bisphenol-based flame retardants, from the viewpoint of flame retardance and compatibility with the styrene-based resin.

[0028]

Examples of brominated bisphenol-based flame retardants include, but are not limited to, tetrabromobisphenol A, tetrabromobisphenol A-bis(2,3-dibromopropyl ether), tetrabromobisphenol A-bis(2,3-dibromo-2methylpropyl ether), tetrabromobisphenol S, tetrabromobisphenol S-bis(2,3-dibromopropylether), tetrabromobisphenol S-bis(2,3-dibromo-2-methylpropyl ether), tetrabromobisphenol F, tetrabromobisphenol F-bis(2,3-dibromopropyl ether), tetrabromobisphenol F-bis(2,3-dibromo-2-methylpropyl ether)tetrabromobisphenol A-bis(allyl ether), tetrabromobisphenol A polycarbonate oligomer and tetrabromobisphenol A oligomer epoxy group addition products. Particularly preferred among brominated bisphenol-based flame retardants are tetrabromo bisphenol A bis(2,3-dibromopropyl ether) and tetrabromobisphenol A-bis(2,3-dibromopropyl ether), because they are resistant to decomposition during kneading with styrenic copolymers, and tend to readily exhibit a high flame-retardant effect. Using tetrabromobisphenol A-bis(2,3-dibromopropyl ether) and tetrabromobisphenol A-bis(2,3-dibromo-2methylpropyl ether) in combination is more preferred as it will tend to result in excellent flame retardance and thermostability.

[0029]

A bromine-based flame retardant preferably also employs in combination a brominated isocyanurate-based flame retardant as a flame-retardant aid. Examples of brominated isocyanurate-based flame retardants include, but are not limited to, mono(2,3-dibromopropyl) isocyanurate, di(2,3-dibromopropyl) isocyanurate and tris(2,3-dibromopropyl) isocyanurate, mono(2,3,4-tribromobutyl) isocyanurate, di(2,3,4-tribromobutyl) isocyanurate and tris(2,3,4-tribromobutyl)isocyanurate. A particularly preferred brominated isocyanurate is tris(2,3-dibromopropyl) isocyanurate, because it exhibits a very high flame retardance effect.

[0030]

The content of the bromine-based flame retardant is preferably 0.1 part by weight to 10 parts by weight, more preferably 1 part by weight to 9 parts by weight and more preferably 2

parts by weight to 8 parts by weight, with respect to 100 parts by weight of the styrenic copolymer in the extruded foam sheet. If it is 0.1 part by weight or greater a sufficient level of flame retardance will tend to be ensured, and if it is no greater than 10 parts by weight an adequately satisfactory level of moldability will tend to be exhibited during production of an extruded foam sheet.

[0031]

<Production method for styrenic copolymer>

<Polymerization step>

The polymerization method for the styrenic copolymer of this embodiment may be a known styrene polymerization method such as bulk polymerization, solution polymerization or suspension polymerization, for example. These polymerization methods may be either batch polymerization or continuous polymerization methods, but are preferably continuous polymerization methods from the viewpoint of productivity. As an example of a continuous bulk polymerization method, the monovinyl compound, the conjugated divinyl compound, a solvent as necessary, the polymerization catalyst and the chain transfer agent are added and mixed, to prepare a starting solution containing the monomers. According to one method, the starting solution is continuously fed into an apparatus provided with one or more reactors arranged in series and/or in parallel, and a devolatilizing apparatus for a devolatilizing step which removes the volatile components such as unreacted monomer, and polymerization is conducted in a stepwise manner.

[0032]

The reactors may be, for example, complete mixing reactors, laminar flow reactors, or loop reactors in which polymerization is conducted while removing out a portion of the polymerization solution. There is no particular restriction on the order of arrangement of the reactors.

[0033]

During polymerization of the styrenic copolymer of this embodiment, a polymerization solvent, a polymerization initiator such as an organic peroxide, and a chain transfer agent, may be used as necessary from the viewpoint of controlling the polymerization reaction. The polymerization solvent is usually used to adjust the polymerization rate and molecular weight in continuous bulk polymerization and continuous solution polymerization. The polymerization solvent is not particularly restricted, and examples include benzene, alkylbenzenes such as toluene, ethylbenzene and xylene, ketones such as acetone and methyl ethyl ketone, and aliphatic hydrocarbons such as hexane and cyclohexane. The amount of polymerization solvent used is not particularly restricted, but from the viewpoint of controlling gelation, improving productivity and increasing the molecular weight, in most cases it is preferably 1 to 50 wt% and more

preferably 3 to 20 wt% with respect to the mixed solution composition comprising all of the monomers, polymers and solvent in the polymerization reactor.

[0034]

When the polymerization material is polymerized to obtain the styrenic copolymer of this embodiment, a polymerization initiator and chain transfer agent may also be added to the polymerization material composition. The polymerization initiator is not particularly restricted, and examples of organic peroxides include peroxy ketals such as 2,2-bis(t-butylperoxy)butane, 1,1-bis(t-butylperoxy)cyclohexane and n-butyl-4,4-bis(t-butylperoxy) valerate, dialkyl peroxides such as di-t-butyl peroxide, t-butylcumyl peroxide and dicumyl peroxide, diacyl peroxides such as acetyl peroxide and isobutyryl peroxide, peroxydicarbonates such as diisopropyl peroxydicarbonate, peroxy esters such as t-butyl peroxyacetate, ketone peroxides such as acetylacetone peroxide, and hydroperoxides such as t-butyl hydroperoxide. The polymerization initiator is preferably used at 0.005 to 0.08 wt% with respect to the monovinyl compound. The chain transfer agent is not particularly restricted, and examples include α -methylstyrene dimer, n-dodecylmercaptane, t-dodecylmercaptane and n-octylmercaptane. The chain transfer agent is preferably used at 0.01 to 0.50 wt% with respect to the monovinyl compound.

[0035]

For this embodiment, a phenol-based thermal degradation inhibitor is preferably added in the polymerization step or devolatilizing step, or after the polymerization step and before the devolatilizing step. The phenol-based thermal degradation inhibitor is more preferably added after completion of the polymerization step (preferably immediately after) and before the devolatilizing step.

[0036]

Examples of phenol-based thermal degradation inhibitors include 2-t-butyl-6-(3-t-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (trade name: SUMIRIZER GM by Sumitomo Chemical Co., Ltd.) and 2-[1-(2-hydroxy-3,5-di-t-phenylpentyl)ethyl]-4,6-di-t-phenylpentyl acrylate (trade name: SUMIRIZER GS, by Sumitomo Chemical Co., Ltd.). The addition amount is 0.01 to 0.5 wt%, preferably 0.02 to 0.3 wt% and more preferably 0.03 to 0.2 wt%, with respect to the styrenic copolymer at the outlet of the final reactor.

[0037]

If the amount of phenol-based thermal degradation inhibitor added is 0.01 wt% or greater, it will be possible to more effectively minimize production of the monovinyl compound and its dimers or trimers, in the devolatilizing step. On the other hand, adding the phenol-based thermal degradation inhibitor in an amount of greater than 0.5 wt% does not provide a sufficient effect of minimizing production of the monovinyl compound and its dimers or trimers.

[0038]

<Devolatilizing step>

As an example for the devolatilizing apparatus, any common devolatilizing apparatus may be used such as a flash drum, twin-screw devolatilizer, thin-film evaporator or extruder, and usually a heater-equipped vacuum devolatilizing tank or volatilizing extruder is used. Examples
5 for the arrangement of the devolatilizing apparatus include using only a single heater-equipped vacuum devolatilizing tank, using two heater-equipped vacuum devolatilizing tanks connected in series, and using a heater-equipped vacuum devolatilizing tank and a volatilizing extruder connected in series. In order to reduce volatile components to an absolute minimum, it is preferred to use two heater-equipped vacuum devolatilizing tanks connected in series, or a
10 heater-equipped vacuum devolatilizing tank and a volatilizing extruder connected in series.

[0039]

The conditions for the devolatilizing step are not particularly restricted, and for example, when polymerization of the styrenic copolymer is carried out by bulk polymerization, the polymerization may be carried out to a final unreacted monovinyl compound content of
15 preferably no greater than 50 wt% and more preferably no greater than 40 wt% in the styrenic copolymer. Devolatilizing treatment can remove the volatile components such as the unreacted substance (monovinyl compound) and/or solvent.

[0040]

The temperature for the devolatilizing treatment will usually be about 190 to 280°C. The
20 pressure for the devolatilizing treatment is preferably 0.1 to 50 kPa, more preferably 0.13 to 13 kPa, even more preferably 0.13 to 7 kPa and most preferably 0.13 to 1.3 kPa. The devolatilizing method is preferably, for example, a method of devolatilizing under reduced pressure while heating, or a method of devolatilizing through an extruder designed to remove the volatile components.

[0041]

<Production method for extruded foam sheet>

The production method for an extruded foam sheet according to this embodiment may be an extrusion method in which the styrenic copolymer of this embodiment is melt kneaded in an extruder, together with other compounds if necessary, and such methods include, but are not
30 limited, to the following. First, the styrenic copolymer of this embodiment is melt kneaded in an extruder connected to a circular die, and the melt kneaded mixture is extruded in a foamed state through a toric opening provided at the front end of the circular die, to form a cylindrical foam body. Next, a commonly known method is employed in which the foam body is placed in sliding contact with the outer peripheral surface of a cooling mandrel having a larger diameter than the
35 opening of the circular die, to cool it while stretching it in the circumferential direction, and it is consecutively cut along the direction of extrusion and allowed to expand.

[0042]

The foaming agent and foam nucleating agent used for extrusion foaming may be commonly used substances. The foaming agent is not particularly restricted, and examples include butane, pentane, freon, carbon dioxide, nitrogen and water, with butane being preferred. The foam nucleating agent is also not particularly restricted, and talc, for example, may be used. Preferably, the thickness of the extruded foam sheet for this embodiment is 0.5 mm to 5.0 mm, the apparent density is 50 g/L to 300 g/L and the basis weight is 80 g/m² to 300 g/m². A film may be laminated on the extruded foam sheet. The type of film used may generally be polystyrene.

[0043]

<Molded article>

The molded article of this embodiment is a secondary molded article produced by using the extruded foam sheet of the embodiment. The extruded foam sheet of this embodiment may be subjected to secondary molding by a conventional publicly known method such as vacuum forming, pneumatic forming, vacuum pressure forming, double-sided vacuum forming or press molding, to form a secondary molded article such as a tray, cup, rice bowl or natto bowl. Examples of secondary molded articles for this embodiment include food tray containers with a length of 5.5 to 21 cm, a width of 6.5 to 36 cm and a depth of 1.1 to 3.4 cm, and soup or rice bowls with a length of 3.5 to 20 cm, a width of 3.5 to 20 cm and a depth of 2.0 to 20 cm, formed with a vacuum forming machine using an extruded foam sheet of this embodiment as the molding material, with the transverse direction as the direction of extrusion. The temperature conditions for vacuum forming are usually preferred to be 120 to 150°C, although this is not limitative.

[0044]

(Monovinyl compound residue in extruded foam sheet)

The monovinyl compound residue in the extruded foam sheet of this embodiment is preferably no greater than 100 ppm. If the monovinyl compound residue in the extruded foam sheet is no greater than 100 ppm, this is preferred as it will tend to result in deep drawing moldability, as well as a highly superior outer appearance for the molded article.

[0045]

The styrenic copolymer of this embodiment can yield products with excellent formability, low gelatinous material and consequently an excellent outer appearance. Molding methods that are suitable for use include injection molding, extrusion molding, vacuum forming, pneumatic forming, extrusion foam molding, calender molding and blow molding, and a variety of molded articles can be obtained for a wider range of uses than the prior art.

EXAMPLES

[0046]

Embodiments of the invention will now be explained in detail through examples and comparative examples, with the understanding that these examples are not limitative on the invention.

[0047]

<Methods of measurement and evaluation>

The methods of measurement and evaluation were as follows.

[0048]

(1) Measurement of molecular weight

The number-average molecular weight (M_n) of the conjugated divinyl compounds, and the weight-average molecular weight (M_w), Z-average molecular weight (M_z), proportion of molecular weight 1,000,000 or greater and proportion of molecular weight of 2,000,000 or greater of the styrenic copolymers were measured by gel permeation chromatography (GPC).

Measurement was performed under the following conditions.

Apparatus: HLC-8220 by Tosoh Corp.

Fractionation column: Two TSK gel Super HZM-H (inner diameter: 4.6 mm) by Tosoh Corp., connected in series

Guard column: TSK guard column Super HZ-H by Tosoh Corp.

Measuring solvent: Tetrahydrofuran (THF)

Sample dissolution: After dissolving 5 mg of measuring sample in 10 mL of solvent, filtration was carried out with a 0.45 μ m filter.

Injection rate: 10 μ l

Measuring temperature: 40°C

Flow rate: 0.35 mL/min

Detector: Ultraviolet absorption detector (UV-8020, wavelength of 254 nm)

Eleven types of TSK standard polystyrene (F-850, F-450, F-128, F-80, F-40, F-20, F-10, F-4, F-2, F-1, A-5000) by Tosoh Corp. were used to construct a calibration curve. The calibration curve was constructed using a first-order approximation.

[0049]

(2) Measurement of melt mass-flow rate (MFR)

The melt mass-flow rate of the styrenic copolymer was measured according to ISO1133, under conditions of 200°C, 49 N load.

[0050]

(3) Evaluation of gelatinous material in solid sheet

A 30 mm ϕ sheet extruder (product of Soken Co., Ltd.) was used for extrusion of the

styrenic copolymer, to fabricate a 0.5 mm-thick sheet (solid sheet). Twenty test pieces with a size of 100 mm length $\times$ 100 mm width were cut out from the obtained sheet, and gelatinous materials with an average short diameter and long diameter of 2 mm or greater were visually determined. For the assessment, “VG” represents 0-2, “G” represents 3-10 and “P” represents 11 or more test pieces containing gelatinous material.

[0051]

(4) Measurement of initial rise strain, maximum rise strain and maximum rise ratio

Measurement of the initial rise strain, maximum rise strain and maximum rise ratio of the styrenic copolymer was carried out based on the following viscoelasticity measurement method.

Apparatus: ARES-G2 viscoelasticity meter (product of TA Instruments)

Measuring system: ARES-EVF option

Test piece dimensions: 20 mm length, 0.7 mm thickness, 10 mm width

Elongation strain rate: 0.01/sec

Temperature: 150°C

Measuring atmosphere: nitrogen airflow

Preheating time: 2 minutes

Pre-elongation strain rate: 0.03/sec

Pre-elongation length: 0.295 mm

Relaxation time after pre-elongation: 2 minutes

The viscoelasticity was measured by attaching the test piece to a roller and stabilizing the temperature to the measuring temperature, and then allowing it to stand for preheating, for the specified preheating time. After preheating was complete, pre-elongation was carried out under the conditions described above. After pre-elongation, it was allowed to stand for 2 minutes, the stress produced during the pre-elongation was relaxed, and measurement was taken.

[0052]

The maximum rise strain is the Hencky strain at which the extensional viscosity was maximum in the viscoelasticity measurement described above.

The initial rise strain was also calculated by the following method. Based on the results obtained from the viscoelasticity measurement, both common logarithm graphs were drawn by plotting Hencky strain on the abscissa and extensional viscosity on the ordinate, and a power approximation curve was drawn with the linear region as the Hencky strain range of 0.2 to 0.5 (see the broken line in Fig. 1, for example). When strain hardening occurs, the measured extensional viscosity (which is the extensional viscosity defined as the extensional viscosity in the nonlinear region) is higher than the extensional viscosity on an approximate straight line extrapolated from the linear region (which is the extensional viscosity defined as the extensional viscosity in the linear region). For the same Hencky strain, the initial rise strain was recorded as

the Hencky strain when the difference between the extensional viscosity in the nonlinear region and the extensional viscosity in the linear region was 3% of the extensional viscosity in the nonlinear region. The maximum rise ratio was calculated as (extensional viscosity in nonlinear region of maximum rise strain/extensional viscosity in linear region of maximum rise strain).

[0053]

(5) Method of evaluating deep drawing moldability of solid sheet

A 30 mm ϕ sheet extruder (product of Soken Co., Ltd.) was used for extrusion of the styrenic copolymer, to fabricate a 0.5 mm-thick sheet (solid sheet). A 250 mm long $\times$ 250 mm wide size was cut out from the obtained sheet, and using a sheet container molding machine by Soken Co., Ltd., the sheet was fitted on a fixed frame in the sheet molding machine, and heating was performed for 20 seconds with the mean temperature of the heater set to 220°C and the atmosphere temperature set to 110°C. The entire fixed frame was then slid over a rice bowl die having a diameter of 10 cm and a depth of 10 cm (temperature: 40°C), and vacuum forming was carried out, to form 20 molded articles. Absence of tearing in the side of each molded article was visually confirmed, and the number of molded articles that were moldable without tearing was recorded as an index of the deep drawing moldability.

[0054]

(6) Measurement of monovinyl compound residue in extruded foam sheet

A styrene-based resin composition was obtained by adding 0.15 part by weight of talc (mean particle size: 1.3 μ m) as a foam nucleating agent and 4 parts by weight of liquefied butane as a foaming agent, with respect to 100 parts by weight of a styrenic copolymer. An extrusion foaming machine equipped with a circular die having a diameter of 150 mm was used for extrusion foam molding of the styrene-based resin composition. The temperature in the resin melting zone of the extrusion foaming machine was adjusted to 200 to 230°C, the rotary cooler temperature to 130 to 170°C, and the die temperature to 145°C. Immediately after extrusion foaming, the foam body was cooled with a cooling mandrel and cut with a cutter at one point on the circumference, to obtain an extruded foam sheet with a sheet thickness of 1.4 mm and a width of 1,000 mm.

The monovinyl compound residue in the extruded foam sheet was measured by gas chromatography under the following conditions. A 1 g portion of the extruded foam sheet was dissolved in 25 ml of dimethylformamide to prepare a measuring sample.

Measuring conditions

Detection method: FID

Device: GC14B by Shimadzu

Column: CHROMAPACK CP WAX 52CB

100 m, 2 μ m film thickness, 0.52 mm ϕ

Column temperature: Holding at 110°C for 10 minutes, raising to 130°C at 15°C/min, holding at 130°C for 2 minutes.

Inlet temperature: 150°C

Detector temperature: 150°C

5 Carrier gas: Helium

[0055]

(7) Deep drawing moldability of extruded foam sheet

The extruded foam sheet was left to stand for 20 days at $23 \pm 3^\circ\text{C}$, $50 \pm 5\%$ relative humidity. Next, using a sheet container molding machine by Soken Co., Ltd., the foamed sheet was fitted on a fixed frame in the sheet molding machine, and heating was performed for 15 seconds with the mean temperature of the heater set to 200°C and the atmosphere temperature set to 130°C . The entire fixed frame was then slid over a cup-shaped die having a diameter of 10 cm and a depth of 6 cm (temperature: 40°C), and vacuum forming was carried out, to form 100 molded articles. Absence of tearing in the side of each molded article was visually confirmed, and the number of molded articles that were moldable without tearing was recorded as an index of the deep drawing moldability.

[0056]

(8) Examination and method of assessing outer appearance of molded article

The gloss and surface roughened states of the deep drawn molded article surfaces of the extruded foam sheets molded in (6) above were visually confirmed.

G: Good (uniform)

F: Fair (Non-uniform: liquid drip marks confirmed on only one side (a side surface or the bottom) of the molded article

P: Poor (Non-uniform: liquid drip marks confirmed on all sides (the side surfaces and bottom) of the molded article

[0057]

(9) Foam body density

The foam body density of each extruded foam sheet was measured based on ISO10350. The measuring apparatus used was a densitometer (SGM-220-60 meter) by Shimadzu Corp.

30 **[0058]**

(10) Expansion ratio

The expansion ratio was calculated by the following formula, using the value of the foam body density determined in (9) above (ρ_f) and the density of the styrenic copolymer (ρ).

Expansion ratio = ρ/ρ_f

35 **[0059]**

<Conjugated divinyl compound production example>

Conjugated divinyl compounds 1, 5 and 6 were produced by the following method.

[0060]

<Conjugated divinyl compound 1>

In a 5 L-volume reactor equipped with a stirrer, thermometer and reflux condenser there were charged 2742 g of polybutadiene with a hydroxyl group at both ends (polybutadiene diol) (Mn: 1900), 379 g of methyl acrylate, 380 g of n-hexane, 0.8194 g of hydroquinonemonomethyl ether and 0.5533 g of 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl. The obtained mixture was passed through a calcium chloride tube while blowing air into the mixture, for reflux dewatering at 80 to 85°C. The water in the mixture was measured by the Karl Fischer method, whereby the water content was confirmed to be no greater than 200 ppm. Next, 1.3685 g of tetra-n-butyl titanate was added to the mixture as a transesterification catalyst, and the generated methanol was distilled off out of the reaction system under circulation of n-hexane as an azeotropic solvent, while conducting reaction for 10 hours at a reaction temperature of 80 to 85°C, with stirring.

[0061]

Next, the temperature in the reactor was adjusted to 75 to 80°C, and concentration was carried out to a pressure reduction of 70 to 2 kPa until at least 95% of the methyl acrylate and n-hexane used were distilled off, recovering the excess methyl acrylate and n-hexane. To 2070 g of the obtained polybutadiene with an acryl group at both ends (polybutadiene diacrylate) there were added 2000 g of toluene, 200 g of acetone, 20 g of ion-exchanged water and 20 g of hydrotalcite (compositional formula: $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) [product of Kyowa Chemical Industry Co., Ltd., trade name: KYOWAAD 500PL] as a transesterification catalyst, and treatment was carried out at 75 to 80°C for 2 hours. The temperature in the reactor was then adjusted to 75 to 80°C, and concentration was performed with pressure reduction to 90 to 35 kPa to recover 400 g of a mixed distillate comprising toluene, acetone and water, the obtained concentrate was filtered under air pressurization to separate the catalyst and the adsorbent, and deaeration of the solvent was further carried out at a temperature of 60 to 80°C and pressure reduction of 30 to 0.8 kPa, to obtain conjugated divinyl compound 1.

[0062]

The conversion rate of the polybutadiene with an acryl group at both ends to conjugated divinyl compound 1 was measured to be 99.3%, by high-performance liquid chromatography (HPLC). The number-average molecular weight (Mn) in terms of polystyrene was 1900, as measured by GPC.

[0063]

<Conjugated divinyl compound 5>

Conjugated divinyl compound 5, produced under the same conditions except for

changing the molecular weight of the polybutadiene with a hydroxyl group at both ends to Mn: 25,000, had a conversion rate from polybutadiene with an acryl group at both ends of 99.5%. The number-average molecular weight (Mn) in terms of polystyrene was 26,000, as measured by GPC.

5 **[0064]**

<Conjugated divinyl compound 6>

Conjugated divinyl compound 6, produced under the same conditions except for changing the molecular weight of the polybutadiene with a hydroxyl group at both ends to Mn: 57,000, had a conversion rate from polybutadiene with an acryl group at both ends of 99.2%. The number-average molecular weight (Mn) in terms of polystyrene was 58,000, as measured by GPC.

10 **[0065]**

<Example 1>

A starting solution was prepared by adding 80 parts by weight of styrene, 20 parts by weight of ethylbenzene, 0.035 part by weight of conjugated divinyl compound 1 (polybutadiene with acrylate at ends, Mn: 1900) (2.4×10^{-5} mol per mole of styrene) and 0.030 part by weight of 2,2-bis(4,4-di-tertiary-butylperoxycyclohexyl)propane [PERTETRA A, product of NOF Corp.], as a polymerization initiator 1. The prepared starting solution was continuously supplied at a rate of 1.00 L/hr to a complete-mixing first reactor with an internal volume of 5.4 L, held at a temperature of 105°C. The polymerization solution was then supplied from the first reactor to a plug flow-type second reactor with an internal volume of 3 L, in the order in which the starting solution passed through. At the second reactor, the temperatures in 3 zones were kept at 119, 133 and 143°C. In the second zone, 0.03 part by weight of 1,1-di-(tertiary-butylperoxy)cyclohexane [PERHEXA C, product of NOF Corp.] was added as polymerization initiator 2. The polymerization solution was then supplied from the second reactor to a vacuum degasser that had been heated to a temperature of 240°C, removing the volatile components such as unreacted monomer and solvent, and after 72 hours of continuous operation, a styrenic copolymer for evaluation was obtained.

The production conditions and analysis results for the styrenic copolymer are shown in Table 1. Conjugated divinyl compound 1 was also synthesized by the method described in the production example. The number-average molecular weight (Mn) is the value in terms of polystyrene, measured by GPC. The number of moles of conjugated divinyl compound per mole of styrene (monovinyl compound) is the value measured using ^1H -NMR and ^{13}C -NMR. The measuring apparatus used was a JEOL-ECA500 by JEOL Corp. The solvent used was chloroform-d₁, and the resonance line for tetramethylsilane was used as the internal standard.

35 **[0066]**

Examples 2 to 14 and Comparative Examples 1 to 6 were carried out in the same manner as Example 1, except for changing the conditions as shown in Tables 1 and 2, and the Mw, Mz/Mw, proportion of molecular weight 1,000,000 or greater, proportion of molecular weight of 2,000,000 or greater, initial rise strain and maximum rise ratio for each styrene copolymer were controlled to the values listed in Tables 1 and 2.

[0067]

The conjugated divinyl compounds, polymerization initiators and thermal degradation inhibitors listed in the tables were as follows. Conjugated divinyl compounds 2 to 9, 11 and 12 had conjugated vinyl groups at both of the furthest ends of the molecule.

Conjugated divinyl compound 2: Polybutadiene diacrylate [CN307 by Tomoe Engineering Co., Ltd.], Mn: 3800

Conjugated divinyl compound 3: Polybutadiene with acrylate at ends [BAC-45 by Osaka Organic Chemical Industry, Ltd.], Mn: 4800

Conjugated divinyl compound 4: Urethane acrylate oligomer [CN9014NS by Tomoe Engineering Co., Ltd.], Mn: 8000

Conjugated divinyl compound 7: Aromatic urethane acrylate [CN9782 by Tomoe Engineering Co., Ltd.], Mn: 5200

Conjugated divinyl compound 8: Reaction product of (2,2',3,3',5,5'-hexamethylbiphenyl-4,4'-diol·2,6-dimethylphenol polycondensate) and chloromethylstyrene [OPE-2ST by Mitsubishi Gas Chemical Co., Inc.], Mn: 1200

Conjugated divinyl compound 9: 1,3-Butylenediol dimethacrylate [product of Wako Pure Chemical Industries, Ltd.], molecular weight: 226

Conjugated divinyl compound 10: NK ester A-GLY-20E [product of Shin-Nakamura Chemical Co., Ltd.], molecular weight: 1295, average number of conjugated vinyl groups per molecule of conjugated divinyl compound 10 = 3.

Conjugated divinyl compound 11: Divinylbenzene [product of Wako Pure Chemical Industries, Ltd.], molecular weight: 130

Conjugated divinyl compound 12: Polyethyleneglycol dimethacrylate [product of Sigma-Aldrich Japan, KK.], molecular weight: 750

Polymerization initiator 2: 1,1-di-(tertiary-Butylperoxy)cyclohexane [PERHEXA C by NOF Corp.]

Thermal degradation inhibitor 1: 2-[1-(2-Hydroxy-3,5-di-*t*-phenylpentyl)ethyl]-4,6-di-*t*-phenylpentyl acrylate [SUMIRIZER GS by Sumitomo Chemical Co., Ltd.]

Thermal degradation inhibitor 2: Octadecyl-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)-propionate [IRGANOX 1076 by Ciba Specialty Chemicals, Inc.]

[0068]

The measurement and evaluation results for Examples 2 to 14 and Comparative Examples 1 to 6 are summarized in Tables 1 and 2. As shown in Fig. 1, the styrenic copolymer of Example 4 exhibited strain hardening during ARES-EVF measurement.

[0069]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Starting materials	Starting material supply flow rate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Styrene	80.0	80.0	78.0	80.0	80.0	87.0	87.0	80.0	80.0	80.0
	Ethylbenzene	20.0	20.0	22.0	20.0	20.0	13.0	13.0	20.0	20.0	20.0
	Type of conjugated divinyl compound	1	2	3	3	4	5	6	7	3	3
	Addition amount of conjugated divinyl compound	0.035	0.117	0.058	0.222	0.246	0.653	0.653	0.600	0.222	0.222
First reactor	Number of moles of conjugated divinyl compound added per mole of styrene	2.4×10^{-5}	4.0×10^{-5}	1.6×10^{-5}	6.0×10^{-5}	4.0×10^{-5}	3.0×10^{-5}	1.3×10^{-5}	1.5×10^{-4}	6.0×10^{-5}	6.0×10^{-5}
	Polymerization initiator 1	0.030	0.030	0.030	0.030	0.030	-	0.030	0.030	0.030	0.030
	Polymerization initiator 2	-	-	-	-	-	0.030	-	-	-	-
	Temperature	105	105	105	105	105	102	102	105	105	105
	Outlet solid concentration	35	34	33	35	35	35	35	34	35	35
Second reactor	Zone 1 temperature	119	122	123	119	119	115	112	119	120	120
	Zone 2 temperature	133	133	137	132	132	127	125	132	125	125
	Zone 3 temperature	143	143	147	142	142	137	138	142	130	130
	Final solid concentration	64	65	64	63	63	65	64	65	65	65
	Zone 2 Amount of polymerization initiator 2 added	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Devolatilizing conditions	Zone 3 Amount of thermal degradation inhibitor 1 added	-	-	-	-	-	-	-	-	0.16	-
	Zone 3 Amount of thermal degradation inhibitor 2 added	-	-	-	-	-	-	-	-	-	0.16
	Temperature	240	240	240	240	240	240	240	240	240	240
	Pressure	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0
	Number of moles of conjugated divinyl compound per mole of styrene	3.8×10^{-5}	6.2×10^{-5}	2.5×10^{-5}	9.5×10^{-5}	6.3×10^{-5}	4.6×10^{-5}	2.1×10^{-5}	2.3×10^{-4}	9.5×10^{-5}	9.5×10^{-5}
Styrenic copolymer properties	Mw	29.7	32.2	27.0	36.9	33.3	30.2	31.5	40.5	39.8	38.0
	Mz/Mw	2.10	2.46	2.18	2.95	3.07	4.56	4.66	4.28	3.0	2.8
	Proportion of molecular weight 1,000,000 or greater	6.97	7.43	5.22	9.75	7.94	6.51	7.11	11.75	11.3	10.4
	Proportion of molecular weight 2,000,000 or greater	1.25	1.58	1.18	2.18	2.04	2.75	2.93	3.46	2.82	2.36
	Total amount of styrene dimers and trimers	2810	2820	2850	2780	2750	2650	2630	2880	1480	2050
Solid sheet properties	MFR	1.58	1.64	1.47	1.26	1.68	2.42	2.21	0.84	0.95	1.10
	Initial rise strain	1.00	0.71	0.70	0.65	0.61	0.59	0.55	0.61	0.54	0.58
	Maximum rise ratio	1.34	1.68	1.38	1.75	1.50	1.38	1.47	2.45	2.35	1.78
	Gelatinous material in sheet	VG	VG	VG	VG	VG	VG	G	G	VG	VG
	Deep drawing moldability	13	15	13	15	14	13	9	15	19	16
Extruded foam sheet properties	Expansion ratio	14.3	14.7	14.5	15.4	14.9	15.9	14.8	15.1	14.9	15.5
	Residual amount of styrene monomer	197	200	202	199	196	193	190	220	85	99
	Total amount of styrene dimers and trimers	2870	2890	2910	2820	2810	2740	2710	2930	1520	2110
	Deep drawing moldability	83	91	88	96	93	89	90	100	100	100
	Outer appearance assessment	F	F	F	F	F	F	F	P	G	G

[0070]

[Table 2]

			Example 11	Example 12	Example 13	Example 14	Comp. Example 1	Comp. Example 2	Comp. Example 3	Comp. Example 4	Comp. Example 5	Comp. Example 6
			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Starting materials	Starting material supply flow rate	L/hr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Styrene	pbw	80.0	80.0	87.0	80.0	86.0	74.0	80.0	80.0	80.0	80.0
	Ethylbenzene	pbw	20.0	20.0	13.0	20.0	14.0	26.0	20.0	20.0	20.0	20.0
	Type of conjugated divinyl compound	-	3	8	3	3	3	3	9	10	11	12
	Addition amount of conjugated divinyl compound	pbw	0.333	0.055	0.333	0.222	0.004	0.854	0.024	0.144	0.015	0.043
	Number of moles of conjugated divinyl compound added per mole of styrene		9.0×10^{-5}	6.0×10^{-5}	9.0×10^{-5}	6.0×10^{-5}	1.1×10^{-6}	2.4×10^{-4}	1.6×10^{-4}	1.4×10^{-4}	1.5×10^{-4}	6.0×10^{-5}
First reactor	Polymerization initiator 1	pbw	0.030	0.030	0.030	0.040	0.030	0.030	0.030	0.030	0.030	0.030
	Polymerization initiator 2	pbw		-		-	-	-	-	-	-	-
	Temperature	°C	105	105	102	105	105	105	105	105	105	105
	Outlet solid concentration	wt%	35	35	35	39	38	30	34	34	34	35
	Zone 1 temperature	°C	120	119	120	119	116	130	119	119	110	119
	Zone 2 temperature	°C	125	132	125	133	128	140	133	133	126	132
Second reactor	Zone 3 temperature	°C	130	142	130	143	138	150	143	143	138	142
	Final solid concentration	wt%	65	63	65	68	69	61	65	65	67	63
	Zone 2 Amount of polymerization initiator 2 added	pbw	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	Zone 3 Amount of thermal degradation inhibitor 1 added	pbw	0.16	-	0.16	-	-	-	-	-	-	-
	Zone 3 Amount of thermal degradation inhibitor 2 added	pbw	-	-	-	-	-	-	-	-	-	-
	Temperature	°C	240	240	240	240	240	240	240	240	240	240
Devolatilizing conditions	Pressure	kPa	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0	1.5 to 2.0
	Number of moles of conjugated divinyl compound per mole of styrene		1.4×10^{-4}	9.5×10^{-5}	1.4×10^{-4}	9.5×10^{-5}	1.7×10^{-6}	4.1×10^{-4}	2.5×10^{-4}	2.2×10^{-4}	2.3×10^{-4}	9.5×10^{-5}
Styrenic copolymer properties	Mw	0,000	35	40.6	42	38.0	29.7	-	36.5	49.5	33.3	23.9
	Mz/Mw		2.94	3.00	3.10	2.95	1.92	-	3.59	3.80	4.28	2.28
	Proportion of molecular weight 1,000,000 or greater	%	8.63	10.72	12.27	10.34	6.32	-	9.51	17.55	7.63	4.14
	Proportion of molecular weight 2,000,000 or greater	%	2.11	2.40	3.00	2.24	1.38	-	2.55	6.39	1.34	0.43
	Total amount of styrene dimers and trimers	ppm	1520	2640	1780	2700	3020	-	3210	3350	2640	2670
	MFR	g/10 min	1.40	1.20	0.80	1.10	1.00	-	1.43	0.45	1.43	2.41
Solid sheet properties	Initial rise strain		0.70	0.61	0.79	0.64	-	-	1.82	1.42	0.99	1.95
	Maximum rise ratio		3.79	2.15	5.03	2.10	-	-	1.13	2.36	1.40	1.05
	Gelatinous material in sheet		VG	VG	G	VG	G	P	G	P	P	G
	Deep drawing moldability	number	16	15	8	15	3	0	4	0	0	0
	Expansion ratio	factor	14.2	15.4	14.8	15.4	13.1	Unmoldable	15.4	Unmoldable	14.1	15.8
	Residual amount of styrene monomer	ppm	102	205	110	190	225	-	237	-	183	210
Extruded foam sheet properties	Total amount of styrene dimers and trimers	ppm	1550	2750	1816	2800	3090	Unmoldable	3340	Unmoldable	2730	2812
	Deep drawing moldability	number	100	96	85	96	61	Unmoldable	44	Unmoldable	53	55
	Outer appearance assessment		G	F	P	F	P	Unmoldable	P	Unmoldable	P	P

[0071]

As clearly seen from Tables 1 and 2, in the case of Comparative Example 1, wherein the number of moles of conjugated divinyl compound per mole of the monovinyl compound was as low at 1.7×10^{-6} mol, no strain hardening was exhibited in ARES-EVF measurement. In the case of Comparative Example 2, wherein the number of moles of conjugated divinyl compound per mole of the monovinyl compound was high at 4.1×10^{-4} mol, it was not possible to obtain stabilized data in the ARES-EVF measurement. Moreover, the large amount of THF insoluble portion made measurement impossible in GPC. The sheet also had a large amount of gelatinous material. In Comparative Examples 3 and 6 which had low number-average molecular weights M_n of 226 and 750 for the conjugated divinyl compounds, the initial rise strain was high and the maximum rise ratio was low. In Comparative Example 4 which had 6.39% as the proportion of molecular weight of 2,000,000 or greater, the initial rise strain was high, and the amount of gelatinous material was large. In Comparative Example 5 which had a low number-average molecular weight M_n of 130 for the conjugated divinyl compound, the sheet had a large amount of gelatinous material.

[0072]

In contrast, the styrenic copolymers of Examples 1 to 14, which were styrenic copolymers of a conjugated divinyl compound having a number-average molecular weight (M_n) of 850 to 100,000 and at least one monovinyl compound comprising at least a styrenic compound, wherein the proportion of the conjugated divinyl compound was 2.0×10^{-6} to 4.0×10^{-4} mol per mole of the monovinyl compound, the styrenic copolymer had a weight-average molecular weight (M_w) of 200,000 to 500,000, the ratio of the Z-average molecular weight (M_z) with respect to M_w was 1.8 to 5.0, the proportion of molecular weight 1,000,000 or greater was 4.0% to 20.0% and the proportion of molecular weight of 2,000,000 or greater was 0.3% to 6.0%, and the sheets had low gelatinous material and had suitable physical properties and excellent formability.

[0073]

The embodiments of the invention described above are not intended to place limitations on the invention, and various modifications may be incorporated such as fall within the gist of the invention.

INDUSTRIAL APPLICABILITY

[0074]

The styrenic copolymer of the invention has excellent formability and low gelatinous material, and can therefore be widely used as molding materials for household appliances, office machinery, sundry goods and housing equipment, and as food packaging materials.

CLAIMS

[Claim 1]

A styrenic copolymer of a conjugated divinyl compound having a number-average molecular weight (Mn) of 850 to 100,000 and at least one monovinyl compound comprising at least a styrenic compound, wherein

the content of the conjugated divinyl compound is 2.0×10^{-6} to 4.0×10^{-4} mol, per mole of the monovinyl compound,

the styrenic copolymer has a weight-average molecular weight (Mw) of 200,000 to 500,000, and

the proportion having a molecular weight of 2,000,000 or greater is 0.3% to 6.0%.

[Claim 2]

The styrenic copolymer according to claim 1, wherein the number-average molecular weight (Mn) of the conjugated divinyl compound is 1,000 to 30,000.

[Claim 3]

The styrenic copolymer according to claim 1 or 2, wherein the conjugated divinyl compound has a chain structure.

[Claim 4]

The styrenic copolymer according to any one of claims 1 to 3, wherein conjugated vinyl groups of the conjugated divinyl compound are located at the ends thereof.

[Claim 5]

The styrenic copolymer according to any one of claims 1 to 4, wherein the ratio of the Z-average molecular weight (Mz) with respect to the Mw of the styrenic copolymer is 1.8 to 5.0.

[Claim 6]

The styrenic copolymer according to any one of claims 1 to 5, wherein the proportion of the styrenic copolymer having a molecular weight of 1,000,000 or greater is 4.0% to 20.0%.

[Claim 7]

The styrenic copolymer according to any one of claims 1 to 6, wherein the initial rise strain is 0.2 to 1.3, and the maximum rise ratio is 1.2 to 5.0.

[Claim 8]

The styrenic copolymer according to any one of claims 1 to 7, wherein the conjugated divinyl compound is (hydrogenated) polybutadiene di(meth)acrylate.

[Claim 9]

- 5 The styrenic copolymer according to any one of claims 1 to 8, wherein the total content of styrenic compound dimers and trimers is from 0.01 to 0.30 wt% with respect to 100 wt% of the styrenic copolymer.

[Claim 10]

- 10 A production method for a styrenic copolymer, which includes polymerizing the styrenic copolymer according to any one of claims 1 to 9 using continuous solution polymerization or continuous bulk polymerization.

[Claim 11]

- 15 An extruded foam sheet comprising the styrenic copolymer according to any one of claims 1 to 9 and having a thickness of 0.5 mm to 5.0 mm.

[Claim 12]

- 20 A secondary molded article produced by using the extruded foam sheet according to claim 11.