

Description

Title of Invention:

METHOD FOR PRODUCING STYRENE-BASED RESIN COMPOSITION COMPRISING
HYPERBRANCHED ULTRA-HIGH-MOLECULAR-WEIGHT POLYMER, AND
COMPOSITION

Technical Field

[0001] The present invention relates to a method of manufacturing a styrene-based resin composition formed of a mixture of a hyperbranched ultra-high-molecular-weight component and a linear component obtained by adding and mixing an ethylenically unsaturated monomer including styrene, and a solvent-soluble polyfunctional vinyl copolymer having a plurality of double bonds per molecule, followed by allowing polymerization to proceed, and to a styrene-based resin composition obtained by the manufacturing method.

Background Art

[0002] A styrene-based resin is inexpensive, is excellent in transparency, heat resistance, mechanical strength, and the like, and has satisfactory moldability. Accordingly, the styrene-based resin has been widely used in a large number of fields such as electrical appliances and household articles. These molded articles are obtained by means such as: injection molding; vacuum or pressure forming from a sheet; or blow molding, which involves

extruding a resin from an extruder into a tube form called a parison, clamping the resin into a mold, and then blowing compressed air or the like from its inside. In addition, in order to obtain a molded body having a light weight and heat insulation performance, there is also used a technology such as foam molding. Foam of the styrene-based resin has many features such as lightness in weight, heat-shielding property, and shock-absorbing property, and for example, the following technologies have been widely utilized: sheet-shaped polystyrene paper to be used for food packaging by being thermoformed from polystyrene foam typified by a heat insulation material for residential use into a tray, a bowl, or the like; and bead expansion involving directly impregnating a resin in a particle state, which is obtained by suspension polymerization, with an aliphatic hydrocarbon such as pentane, and forming the resultant into a container by heating such as steam heating. In those molding methods, particularly in molding methods each including a melt drawing process, such as sheet molding, blow molding, and foam molding, there is a strong demand for a material having high strain hardening property at the time of melting.

[0003] Problems in the case of using a resin material having low strain hardening property in the above-mentioned molding methods include the following phenomena. In the sheet molding, when secondary processing into a deep-drawn molded article such as a food container is performed, thickness non-uniformity is liable to be generated in a product owing to a sagging phenomenon involved

in heating and melting, and a crack, rupture, or the like in a product due to insufficient drawability is liable to be generated. In the blow molding, at the time of formation of the parison, low strain hardening property generates drawdown, resulting in difficulty in molding, and a variation in product strength due to thickness non-uniformity is large. Further, in the foam molding, it becomes difficult to allow foam to have fine and closed cells to enhance heat insulation performance. In order to increase a ratio of closed cells in the foam molding, a material capable of being drawn so that no excessively thin portion may be formed in a wall surface at the time of drawing is suitable. A material having low strain hardening property results in small resistance to drawing in a thin-walled region. Accordingly, there is established a negative spiral in which once a thin portion is generated, the portion is further drawn to undergo additional thinning, eventually resulting in rupture of the wall surface. A material having high strain hardening property provides an increased viscosity in the drawn region, thus resulting in higher resistance to drawing in the thin-walled portion than that in a thick-walled portion. Accordingly, the above-mentioned negative spiral is not established, and drawing can be performed with a uniform thickness.

[0004] As means for improving melting characteristics such as a tension and strain hardening property in a molten state, it has long been known that a method involving incorporating an ultra-high-molecular-weight component into a styrene-based resin

composition is effective.

[0005] As a method of obtaining a resin composition containing an ultra-high-molecular-weight component, there has been known a styrene-based polymer composition disclosed in Patent Literature 1, which contains a component having a molecular weight of 2,000,000 or more within a certain range. Although as a method of obtaining this composition, there has been proposed a method involving allowing polymerization to proceed under low temperature by using bulk polymerization or solution polymerization means to produce an ultra-high-molecular-weight component, or mixing an ultra-high-molecular-weight component, which is separately prepared by anionic polymerization, emulsion polymerization, or the like, in a molten state, this method has problems, for example, in that the method is poor in productivity and requires a high cost in the case of blending the separately polymerized component.

[0006] As an approach for avoiding the above-mentioned problems, for example, there is known a styrene-based polymer disclosed in Patent Literature 2, which contains a polyfunctional vinyl compound unit-containing component having a molecular weight of 1,000,000 or more within a certain range. In addition, there is a proposal of performing polymerization by adding an extremely small amount of an aromatic polyfunctional vinyl compound typified by an aromatic divinyl compound to vinyl-based monomers in order to incorporate a branched ultra-high-molecular-weight component. However, when such means is applied to continuous bulk polymerization and the

reaction is continued for a long period of time, a problem arises in that gelation proceeds in a region called a boundary film, in which a flow is stopped, the region being present in a wall surface of a polymerization reactor. An attempt to avoid the problem results in a limitation on an addition amount of the polyfunctional aromatic vinyl compound, which makes it difficult to produce a desired amount of the ultra-high-molecular-weight component. Further, in suspension polymerization, which has a feature in that polymerization is completed to the extent that substantially no unreacted monomer remains, when the proposed polyfunctional vinyl compound is applied as it is, a pendant vinyl group derived from the polyfunctional vinyl compound incorporated into a polymer chain at a latter stage of the polymerization reacts rapidly in a region with a conversion rate of 90% or more, resulting in a significant increase in molecular weight, and hence it is difficult to control a molecular weight and a molecular weight distribution.

[0007] Further, in Patent Literature 3, there is a disclosure of a method involving incorporating an ultra-high-molecular-weight component having a branched structure into a styrene-based polymer through suspension polymerization using a polyfunctional polymerization initiator. In addition, in Patent Literature 4, there is also a disclosure of a method involving incorporating an ultra-high-molecular-weight component having a branched structure into a styrene polymer using a polyfunctional polymerization initiator. In this method, however, the styrene-based polymer as

a whole is liable to have an increased molecular weight, and when a molecular weight modifier such as a chain transfer agent is used in combination to avoid the increase, the effect is liable to be insufficient. In addition, in Patent Literature 5, there is a disclosure of a method involving using a polyfunctional aromatic vinyl compound and a chain transfer agent in combination to control a degree of polymerization of a styrene-based resin. However, this method has problems in that the effect is canceled as in the case of using the polyfunctional initiator, and moreover, when a mercaptan is used as the chain transfer agent, a range of use is limited because of a problem of its peculiar odor.

Citation List

Patent Literature

[0008]

[PTL 1] JP 62-61231 B

[PTL 2] JP 2-170806 A

[PTL 3] JP 7-278218 A

[PTL 4] JP 8-59721 A

[PTL 5] JP 2002-241413 A

Summary of Invention

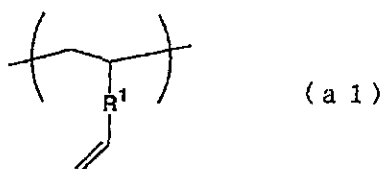
[0009] An object of the present invention is to provide: a method of efficiently manufacturing a styrene-based resin composition free of any gel-like product and containing a hyperbranched

ultra-high-molecular-weight component and a linear component, the styrene-based resin composition having optimal melting characteristics for a processing method that requires a melt drawing process at the time of molding processing such as sheet molding, foam molding, or blow molding; and a styrene-based resin composition obtained by the method, containing a hyperbranched ultra-high-molecular-weight component, the styrene-based resin composition being excellent in melting characteristics.

[0010] That is, the present invention relates to a method of manufacturing a styrene-based resin composition including a hyperbranched ultra-high-molecular-weight copolymer and a linear polymer, the method including adding, to a monovinyl compound including as an essential component styrene, 50 ppm to 5,000 ppm by weight of a solvent-soluble polyfunctional vinyl copolymer having 2 or more vinyl groups per molecule on average and having a branched structure, followed by causing a polymerization reaction to proceed, to obtain a styrene-based resin composition including: a hyperbranched ultra-high-molecular-weight copolymer produced through copolymerization of the solvent-soluble polyfunctional vinyl copolymer and the monovinyl compound; and a linear polymer produced through polymerization of the monovinyl compound.

[0011] In the manufacturing method, a preferred example of the solvent-soluble polyfunctional vinyl copolymer is one that is obtained through polymerization of a divinyl compound and a copolymerizable monovinyl compound, contains a divinyl

compound-derived pendant vinyl group represented by the following formula (a1) at a mole fraction of from 0.05 to 0.50 in a structural unit, and has a ratio between a radius of gyration (nm) at a weight-average molecular weight of the solvent-soluble polyfunctional vinyl copolymer and the mole fraction of from 1 to 100:



in the formula, R¹ represents a divinyl compound-derived hydrocarbon group.

[0012] The present invention also relates to a styrene-based resin composition including a hyperbranched ultra-high-molecular-weight copolymer, which is obtained by the above-mentioned manufacturing method, the styrene-based resin composition including: 2.0 to 20.0 wt% of a hyperbranched ultra-high-molecular-weight copolymer having a weight-average molecular weight of 1,000,000 or more; and 80.0 to 98.0 wt% of a linear styrene-based polymer having a weight-average molecular weight of from 100,000 to 500,000, in which the styrene-based resin composition has a weight-average molecular weight of from 200,000 to 800,000.

Description of Embodiments

[0013] Hereinafter, the present invention is described in detail. As a polymerization method to be used in the present invention, it is suitable to use the so-called continuous bulk polymerization method, which involves: adding and mixing a monovinyl compound including styrene, and a solvent-soluble polyfunctional vinyl copolymer, and as required, a solvent, a polymerization catalyst, a chain transfer agent, and the like; and continuously feeding the monomer and the like to equipment including one or more reactors arranged in tandem and/or parallel and a volatile matter-removing process of removing an unreacted monomer and the like to allow polymerization to proceed gradually. The type of the reactors is exemplified by: a tank type reactor of a complete mixing type; a tower type reactor having plug flow performance; and a loop type reactor configured to extract part of a polymerization liquid while allowing polymerization to proceed. The order of the arrangement of the reactors is not particularly limited, but in order to suppress the generation of a gel-like product in continuous production, it is important to prevent the occurrence of a situation in which the solvent-soluble polyfunctional vinyl copolymer in an unreacted state resides at a high concentration in the boundary film of a reactor wall surface. Accordingly, a tank type reactor of a complete mixing type is preferably selected as a first reactor.

[0014] In addition, as the polymerization method of the present invention, it is also suitable to use the so-called suspension polymerization method, which involves: adding and mixing a monovinyl

compound including styrene, and a solvent-soluble polyfunctional vinyl copolymer, and as required, a polymerization catalyst, a chain transfer agent, and the like; then suspending the mixture in water; and allowing polymerization to proceed. In order to stabilize dispersion, the monomer and the like are fed into water having dissolved therein an organic dispersant such as polyvinyl alcohol or methyl cellulose, or an inorganic dispersant such as tricalcium phosphate or magnesium phosphate, and an anionic surfactant such as sodium dodecylbenzenesulfonate, and are dispersed under stirring, and polymerization is allowed to proceed within the range of from 100 to 150°C. A final polymerization conversion rate at the time of the completion of the reaction is desirably 99% or more, considering the case of, after the completion of the polymerization, directly impregnating an aliphatic hydrocarbon blowing gas such as pentane under pressure while the aqueous dispersion state is kept. When the final polymerization conversion rate is less than 99%, a bad odor is caused significantly in the case where a temperature at the time of secondary molding is equal to or higher than the boiling point of a residual monomer.

[0015] In the present invention, in order to achieve a final polymerization conversion rate of 99% or more, it is desired to: allow polymerization to proceed at a reaction temperature of 120°C or less to a polymerization conversion rate of 50% or more in a raw material solution having added thereto a peroxide-based catalyst whose 1-hr half-life temperature falls within the range of 130±10°C

in an amount of 200 ppm or more with respect to the amount of the raw materials loaded; and then perform polymerization at a reaction temperature higher than the half-life temperature of the catalyst by 5°C or more for 3 hr or more. Through the use of such conditions, a final polymerization conversion rate of 99% or more can be easily achieved without taking an excessively long polymerization time. When the reaction temperature at the latter stage is equal to or lower than the 1-hr half-life temperature, an excessively long polymerization time is required, resulting in a significant reduction in productivity.

[0016] An organic peroxide initiator to be used for achieving a final conversion rate of 99% or more is exemplified by t-butyl peroxyacetate, t-butyl peroxybenzoate, 2,2-di-(t-butylperoxy)butane, or dicumyl peroxide.

[0017] In the present invention, as required, the solvent-soluble polyfunctional vinyl copolymer may be added in the middle of a plurality of reactors in the case of the continuous bulk polymerization, or during the polymerization reaction in the case of the suspension polymerization, in a state of being dissolved in the monovinyl compound, a polymerization solvent, and the like.

[0018] The monovinyl compound including as an essential component styrene to be used in the present invention (hereinafter sometimes referred to as a styrene-based monomer) may contain styrene at 100%, or may be a mixture containing styrene and any other monovinyl compound. Any monovinyl compound may be used as the other monovinyl

compound as long as the compound has an olefinic double bond copolymerizable with styrene. Examples thereof include: aromatic vinyl-based monomers such as p-methylstyrene; acrylic acid monomers such as acrylic acid and methacrylic acid; vinyl cyanide monomers such as acrylonitrile and methacrylonitrile; acrylic monomers such as butyl acrylate and methyl methacrylate; α,β -ethylene unsaturated carboxylic acids such as maleic anhydride and fumaric acid; and imide-based monomers such as phenylmaleimide and cyclohexylmaleimide. One kind of those other monovinyl compounds may be used alone, or two or more kinds thereof may be used in combination. In addition, in order to exploit the characteristics of the styrene-based resin composition, it is preferred that the ratio "styrene:other monovinyl compound" between styrene and the other monovinyl compound be from 20 to 100 mol%:from 0 to 80 mol%.

[0019] The solvent-soluble polyfunctional vinyl copolymer to be used in the present invention (hereinafter sometimes referred to as polyfunctional vinyl copolymer) provides a hyperbranched ultra-high-molecular-weight styrene-based resin by being copolymerized with the styrene-based monomer.

[0020] The polyfunctional vinyl copolymer to be used in the present invention may be obtained in accordance with a method disclosed in JP 2004-123873 A, JP 2005-213443 A, WO 2009/110453, or the like. Specifically, a divinyl compound and at least one or more kinds of monovinyl compounds are used and copolymerized to provide a copolymer having a reactive pendant vinyl group represented

by the formula (a1). Further, as disclosed in the above-mentioned patent literatures, a copolymer having a terminal group other than a vinyl group introduced at a terminal may be used. In particular, a copolymer terminally modified with a compound having an unsaturated bond in the molecule, such as a phenoxy methacrylate, is preferred because the unsaturated bond can act as a crosslinking point in addition to the (a1). In this case, the terminal unsaturated bond-containing structural unit (a2) also has a vinyl group, and hence the total mole fraction (a3) of the structural unit (a2) and the structural unit represented by the formula (a1) represents the total presence amount of vinyl groups.

[0021] The divinyl compound to be used for obtaining the polyfunctional vinyl copolymer is exemplified by: a divinyl aromatic compound typified by divinylbenzene; or an aliphatic or alicyclic (meth)acrylate typified by ethylene glycol di(meth)acrylate.

[0022] In addition, examples of the monovinyl compound to be used in this case include monovinyl compounds including monovinyl aromatic compounds such as styrene as described above.

[0023] Regarding a method of manufacturing the polyfunctional vinyl copolymer, for example, the polyfunctional vinyl copolymer may be obtained by subjecting two or more kinds of compounds selected from divinyl aromatic compounds, monovinyl aromatic compounds, and other monovinyl compounds to cationic copolymerization in the presence of a Lewis acid catalyst and a co-catalyst selected from ester compounds. In addition, in the case of using a

(meth)acrylate-based divinyl or monovinyl compound, the reaction does not proceed by cationic polymerization, and hence the polyfunctional vinyl copolymer may be obtained by performing radical polymerization in the presence of a radical catalyst such as a peroxide.

[0024] The use amounts of the divinyl compound and the monovinyl compound are determined so as to provide the composition of the polyfunctional vinyl copolymer to be used in the present invention. The divinyl compound is used in an amount of preferably from 10 to 90 mol%, more preferably from 30 to 90 mol%, still more preferably from 50 to 90 mol% of all monomers. The monovinyl compound is used in an amount of preferably from 90 to 10 mol%, more preferably from 70 to 10 mol%, still more preferably from 50 to 10 mol% of all monomers. In this case, a substance that acts as a terminal modifier in the cationic polymerization, such as 2-phenoxyethyl methacrylate, is not calculated as a monomer.

[0025] As the Lewis acid catalyst to be used in the manufacture of the polyfunctional vinyl copolymer, a compound formed of a metal ion (acid) and a ligand (base) and capable of accepting an electron pair may be used without any particular limitation. From the viewpoints of the control of a molecular weight and a molecular weight distribution, and polymerization activity, an ether (such as diethyl ether or dimethyl ether) complex of boron trifluoride is most preferably used. The Lewis acid catalyst is used in an amount of from 0.001 to 10 mol, more preferably from 0.001 to 0.01 mol

with respect to 1 mol of all monomers. An excessively large use amount of the Lewis acid catalyst is not preferred because in this case, the polymerization rate increases excessively, and hence it becomes difficult to control the molecular weight distribution.

[0026] An example of the co-catalyst is one or more kinds selected from ester compounds. Of those, ester compounds each having 4 to 30 carbon atoms are suitably used from the viewpoint of the control of the polymerization rate and the molecular weight distribution of the copolymer. From the viewpoint of availability, ethyl acetate, propyl acetate, and butyl acetate are suitably used. The co-catalyst is used in an amount of from 0.001 to 10 mol, more preferably from 0.01 to 1 mol with respect to 1 mol of the monomer compounds. When the use amount of the co-catalyst is excessively large, the polymerization rate decreases, and the yield of the copolymer reduces. On the other hand, when the use amount of the co-catalyst is excessively small, the selectivity of the polymerization reaction reduces, the molecular weight distribution increases, the generation of a gel or the like occurs, and it becomes difficult to control the polymerization reaction.

[0027] In addition, the catalyst to be used in the manufacture of the polyfunctional vinyl copolymer through radical polymerization is exemplified by: an azo-based compound typified by azobisisobutyronitrile; a monofunctional peroxide such as dibenzoyl peroxide or t-butyl peroxybenzoate; or a bifunctional or higher polyfunctional peroxide such as 1,1-bis(t-butylperoxy)cyclohexane.

One kind of those catalysts may be used alone, or two or more kinds thereof may be used in combination.

[0028] The polyfunctional vinyl copolymer to be used in the present invention may be obtained by the manufacturing method as described above, and it is necessary to cause part of the vinyl groups of the divinyl compound to be used as a monomer to remain without being subjected to polymerization. In addition, the number of vinyl groups per molecule on average is controlled to at least 2 or more, preferably 3 or more. The vinyl groups are mainly present as the structural unit represented by the formula (a1). In addition, by causing part of the vinyl groups to remain without being subjected to polymerization, a crosslinking reaction is suppressed, and the polyfunctional vinyl copolymer can be provided with solvent solubility. As used herein, the term "solvent solubility" means that the polyfunctional vinyl copolymer is soluble in toluene, xylene, THF, dichloroethane, or chloroform, and specifically, means that 5 g or more of the polyfunctional vinyl copolymer dissolve in 100 g of any of these solvents at 25°C and no gel is generated. On the other hand, it is necessary that 2 vinyl groups of part of the divinyl compound react to form a crosslink or a branch. With this, a copolymer having a branched structure can be obtained. By causing one of the 2 vinyl groups of part of the divinyl compound to react while causing the other to remain without being subjected to polymerization, and causing the 2 vinyl groups of other part to react as described above, the polyfunctional vinyl copolymer to be used in the present invention

can be obtained. A polymerization method of obtaining such polyfunctional vinyl copolymer is known as described above, and the polyfunctional vinyl copolymer may be manufactured as described above.

[0029] The polyfunctional vinyl copolymer has a weight-average molecular weight (M_w) of preferably from 1,000 to 100,000, more preferably from 5,000 to 70,000. A weight-average molecular weight of less than 1,000 is not preferred because in this case, as in the case of using an aromatic divinyl compound or a polyfunctional (meth)acrylate, a gelation progress-suppressing effect becomes small in the continuous polymerization, and the control of the molecular weight distribution in a high conversion rate region becomes difficult in the suspension polymerization, with the result that a sufficient effect is not obtained.

[0030] A unit containing a vinyl group derived from the divinyl compound introduced into the polyfunctional vinyl copolymer has the structural unit represented by the formula (a1), and the mole fraction of the structural unit (a1) is from 0.05 to 0.50. A mole fraction of less than 0.05 mol is not preferred because in this case, the hyperbranched ultra-high-molecular-weight copolymer is hardly obtained. On the other hand, a mole fraction of more than 0.50 mol is not preferred because in this case, the molecular weight of the hyperbranched ultra-high-molecular-weight copolymer increases excessively, with the result that gelation is liable to occur. In addition, as described above, a copolymer terminally

modified with a compound having an unsaturated bond in the molecule has a vinyl group not only in the structural unit represented by the formula (a1), but also in the terminal unsaturated bond-containing structural unit (a2). Accordingly, the total mole fraction (a3) of both the structural units is desirably from 0.05 to 0.50.

[0031] In addition, the polyfunctional vinyl copolymer preferably has a ratio between a radius of gyration (nm) at its weight-average molecular weight and the mole fraction of the structural unit (a1) or the total mole fraction (a3) of from 1 to 100. In order to prepare the branched ultra-high-molecular-weight component for imparting strain hardening property without causing gelation, the ratio is more preferably from 10 to 80. The case where the ratio is more than 100 is not preferred because the hyperbranched ultra-high-molecular-weight copolymer is hardly obtained, although gelation does not proceed. On the other hand, the case where the ratio is less than 1 is not preferred because the molecular weight of the hyperbranched ultra-high-molecular-weight copolymer increases excessively, with the result that gelation is liable to occur. As used herein, the term "radius of gyration" refers to a value measured by a method described in Examples. It should be noted that the polyfunctional vinyl copolymer is a polymer having a distribution in molecular weight, and naturally, its radius of gyration also has a distribution. Accordingly, the radius of gyration at the weight-average molecular weight is adopted as the

average value of entire radii of gyration.

[0032] The ratio defined herein between the radius of gyration and the mole fraction of the structural unit (a1) or the total mole fraction (a3), which serves as an indicator indicating the double bond content, can be said to be an indicator indicating how many reactive sites are present in the polyfunctional vinyl copolymer serving as a nucleus in the construction of the branched ultra-high-molecular-weight component and how the reactive sites are distributed in the polymerization reaction solution. When the ratio is excessively small, the reactive sites are located close to each other, and hence gelation is liable to be caused. When the ratio is excessively large, it becomes difficult to increase the molecular weight of the branched component.

[0033] The blending ratio of the polyfunctional vinyl copolymer with respect to the styrene-based monomer is preferably from 50 ppm to 5,000 ppm, more preferably from 100 ppm to 3,000 ppm by weight. The case where the blending ratio of the polyfunctional vinyl copolymer is less than 50 ppm is not preferred because the effects of the present invention are unlikely to be sufficiently obtained. On the other hand, in the case of a blending ratio of more than 5,000 ppm, a gel may be generated.

[0034] Through the polymerization of the polyfunctional vinyl compound copolymer and the styrene-based monomer, a styrene-based resin composition of the present invention, which is a mixture of a hyperbranched ultra-high-molecular-weight copolymer (sometimes

referred to as hyperbranched copolymer), which is a copolymer of the polyfunctional vinyl copolymer and the styrene-based monomer, and a linear polymer produced from the styrene-based monomer alone, is obtained. When two or more kinds of monomers are used as the styrene-based monomer, the resultant linear polymer is a copolymer.

[0035] The styrene-based resin composition obtained by the present invention preferably has a weight-average molecular weight (Mw) of from 200,000 to 800,000. When the Mw is less than 200,000, impact strength after processing is insufficient. When the Mw is more than 800,000, the viscosity increases and processability becomes insufficient.

[0036] The styrene-based resin composition as described above contains the hyperbranched copolymer and the linear polymer, and when the styrene-based resin composition is controlled to show the Mw as described above, the hyperbranched copolymer has an ultra-high molecular weight, specifically, an Mw of 1,000,000 or more, and the linear polymer has an Mw of from 100,000 to 500,000. In addition, the ratio between the hyperbranched ultra-high-molecular-weight copolymer having an Mw of 1,000,000 or more and the linear styrene-based polymer having an Mw of from 100,000 to 500,000 is preferably from 2:98 to 20:80. Their ratio may be controlled by adjusting the blending ratio of the polyfunctional vinyl copolymer with respect to the styrene-based monomer and the polymerization conditions.

[0037] In the manufacture of the styrene-based resin

composition, as required, a polymerization solvent, a polymerization initiator such as an organic peroxide, and a chain transfer agent such as an aliphatic mercaptan may be used from the viewpoint of the control of the polymerization reaction.

[0038] The polymerization solvent is used for lowering the viscosity of a reactant in the continuous bulk polymerization. Examples of the organic solvent include toluene, ethylbenzene, xylene, acetonitrile, benzene, chlorobenzene, dichlorobenzene, anisole, cyanobenzene, dimethylformamide, N,N-dimethylacetamide, and methyl ethyl ketone.

[0039] Particularly in the continuous bulk polymerization, when the addition amount of the polyfunctional vinyl copolymer is to be increased, an organic solvent is preferably used from the viewpoint of suppressing gelation as well. With this, the addition amount of the polyfunctional vinyl copolymer described above can be greatly increased, and hence a gel is hardly generated.

[0040] The use amount of the organic solvent is not particularly limited, but from viewpoint of controlling gelation, is generally preferably from 1 to 50 parts by weight, more preferably from 5 to 30 parts by weight with respect to 100 parts by weight of the total amount of the monomer components. A use amount of more than 50 parts by weight is not preferred because in this case, the productivity significantly reduces or the molecular weight of the linear styrene-based resin reduces excessively.

[0041] The polymerization initiator is preferably a radical

polymerization initiator. Examples thereof include known and commonly used radical polymerization initiators such as: a peroxy ketal such as 1,1-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)butane, or 2,2-bis(4,4-di-butylperoxycyclohexyl)propane; a hydroperoxide such as cumene hydroperoxide or t-butyl hydroperoxide; a dialkyl peroxide such as di-t-butyl peroxide, dicumyl peroxide, or di-t-hexyl peroxide; a diacyl peroxide such as benzoyl peroxide or dicinnamoyl peroxide; a peroxy ester such as t-butyl peroxybenzoate, di-t-butyl peroxyisophthalate, or t-butyl peroxyisopropylmonocarbonate; and N,N'-azobisisobutyronitrile, N,N'-azobis(cyclohexane-1-carbonitrile), N,N'-azobis(2-methylbutyronitrile), N,N'-azobis(2,4-dimethylvaleronitrile), and N,N'-azobis[2-(hydroxymethyl)propionitrile]. One kind of those radical polymerization initiators may be used alone, or two or more kinds thereof may be used in combination.

[0042] The chain transfer agent is added to prevent an excessive increase in the molecular weight of the styrene-based resin composition, and a monofunctional chain transfer agent having 1 chain transfer group or a polyfunctional chain transfer agent having a plurality of chain transfer group may be used. Examples of the monofunctional chain transfer agent include alkyl mercaptans and thioglycolic acid esters.

[0043] An example of the polyfunctional chain transfer agent

is one obtained by esterifying a hydroxy group of the following polyhydric alcohol with thioglycolic acid or 3-mercaptopropionic acid: ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, or the like.

Examples

[0044] The present invention is described below more specifically by way of Examples. Measurement methods used are as described below.

[0045] (GPC measurement method)

An average molecular weight in terms of standard polystyrene was measured by high performance liquid chromatography (HLC-8220GPC manufactured by Tosoh Corporation) using an RI detector, TSKgel GMHx1×2, and THF as a solvent under the conditions of a flow rate of 1.0 ml/min and a temperature of 40°C.

[0046] (Double bond quantification method)

Regarding the structural unit (a1), the terminal modifier-derived double bond (a2), and the total mole fraction (a3) of both, structure determination was performed by ¹³C-NMR and ¹H-NMR analysis using a nuclear magnetic resonance spectrometer model JNM-LA600 manufactured by JEOL Ltd. Chloroform-d₁ was used as a solvent, and the resonance line of tetramethylsilane was used as an internal standard.

[0047] (Radius of gyration)

A sample was adjusted to a 0.5% THF solution, which was then filtered through a membrane filter, and the filtrate was subjected to measurement using a GPC/multi-angle light scattering method. Further, the sample was adjusted to a 0.2% THF solution, which was then left to stand for 1 day. After that, the solution was diluted with THF to prepare solutions having four kinds of concentrations (0.02, 0.05, 0.10, and 0.12 wt%), dn/dc measurement was performed using these solutions, and the radius of gyration of the sample was calculated from the resultant dn/dc values.

[0048] (Confirmation of gel-like product)

A flat plate measuring 180 mm×180 mm×3 mm was molded using an injection molding machine, and the presence or absence of a linear mark from a gate portion to be generated in the case of containing a gel-like product was confirmed by visual observation.

[0049] Synthesis Example 1

(Polyfunctional vinyl copolymer α)

3.1 mol (399.4 g) of divinylbenzene, 0.7 mol (95.1 g) of ethylvinylbenzene, 0.3 mol (31.6 g) of styrene, 2.3 mol (463.5 g) of 2-phenoxyethyl methacrylate, and 974.3 g of toluene were fed into a 3.0-L reactor, and were subjected to a reaction for 6.5 hr by adding 42.6 g of boron trifluoride diethyl ether complex at 50°C. The polymerization reaction was quenched with a sodium hydrogen carbonate solution. After that, the oil layer was washed three times with pure water, and the reaction mixed liquid was poured into a large amount of methanol at room temperature to precipitate a polymer.

The obtained polymer was washed with methanol, separated by filtration, dried, and weighed. Thus, 372.5 g of a polyfunctional vinyl copolymer α were obtained. The polyfunctional vinyl copolymer α had a weight-average molecular weight M_w of 8,000, the mole fraction of the divinyl compound-derived vinyl group-containing structural unit (a1) was 0.44, the mole fraction of the 2-phenoxyethyl methacrylate-derived terminal double bond (a2) was 0.03, and the total mole fraction (a3) obtained by adding both was 0.47. In addition, the radius of gyration (r) of the copolymer at the weight-average molecular weight of 8,000 was 6.4 nm. Comparison to the radius of gyration of a linear type at the molecular weight of 8,000, which is 15 nm, reveals that the polyfunctional vinyl copolymer in this synthesis example has a branched structure. In addition, the ratio (r/a3) of the radius of gyration (r) to the mole fraction (a3) is calculated to be 13.6.

[0050] Synthesis Example 2

(Polyfunctional vinyl copolymer β)

2.6 mol (332.0 g) of divinylbenzene, 1.5 mol (198.0 g) of ethylvinylbenzene, 1.1 mol (109.6 g) of styrene, 3.1 mol (630.4 g) of 2-phenoxyethyl methacrylate, and 886.0 g of toluene were fed into a 3.0-L reactor, and were subjected to a reaction for 5.0 hr by adding 35.5 g of boron trifluoride diethyl ether complex at 50°C. The polymerization reaction was quenched with a sodium hydrogen carbonate solution. After that, the oil layer was washed three times with pure water, and the reaction mixed liquid was poured into a

large amount of methanol at room temperature to precipitate a polymer. The obtained polymer was washed with methanol, separated by filtration, dried, and weighed. Thus, 564.0 g of a polyfunctional vinyl copolymer β were obtained. The polyfunctional vinyl copolymer β had an Mw of 5,000, the mole fraction of the divinyl compound-derived vinyl group-containing structural unit (a1) was 0.25, the mole fraction of the 2-phenoxyethyl methacrylate-derived terminal double bond (a2) was 0.02, and the total mole fraction (a3) obtained by adding both was 0.27. In addition, the radius of gyration of the copolymer at the weight-average molecular weight was 8.1 nm. Comparison to the radius of gyration of a linear type at the molecular weight of 5,000, which is 12 nm, reveals that the polyfunctional vinyl copolymer in this synthesis example has a branched structure.

[0051] Synthesis Example 3

(Polyfunctional vinyl copolymer γ)

1.2 mol (159.8 g) of divinylbenzene, 0.7 mol (95.3 g) of ethylvinylbenzene, 2.1 mol (223.2 g) of styrene, 3.1 mol (632.0 g) of 2-phenoxyethyl methacrylate, and 1,082.5 g of toluene were fed into a 3.0-L reactor, and were subjected to a reaction for 6.0 hr by adding 56.8 g of boron trifluoride diethyl ether complex at 50°C. The polymerization reaction was quenched with a sodium hydrogen carbonate solution. After that, the oil layer was washed three times with pure water, and the reaction mixed liquid was poured into a large amount of methanol at room temperature to precipitate a polymer. The obtained polymer was washed with methanol, separated

by filtration, dried, and weighed. Thus, 340.8 g of a polyfunctional vinyl copolymer were obtained. The polyfunctional vinyl copolymer had an Mw of 5,000, the mole fraction of the divinyl aromatic compound-derived vinyl group-containing structural unit (a1) was 0.13, the mole fraction of the 2-phenoxyethyl methacrylate-derived terminal double bond (a2) was 0.01, and the total mole fraction (a3) obtained by adding both was 0.14. In addition, the radius of gyration of the copolymer at the weight-average molecular weight was 10.6 nm. Comparison to the radius of gyration of a linear type at the molecular weight of 5,000, which is 12 nm, reveals that the polyfunctional vinyl copolymer in this synthesis example has a branched structure.

Each of the polyfunctional vinyl copolymers in Synthesis Examples 1 to 3 above was soluble in toluene, xylene, THF, dichloroethane, and chloroform.

[0052] Example 1

85 Parts by weight of styrene, 15 parts by weight of ethylbenzene, and 0.06 part by weight of the polyfunctional vinyl copolymer (α) were homogeneously mixed and then continuously fed at 15 L/hr to continuous bulk polymerization equipment including: two tandem connected tank type reactors each having an internal volume of 30 L and having complete mixing performance; a tower type reactor having an internal volume 15 L, including a built-in static mixer having plug flow performance; and flash chamber type volatile matter-removing equipment including a preheater and a vacuum chamber.

Temperatures were gradually increased to the following temperatures: first reactor: 130°C, second reactor: 140°C, third reactor inlet: 140°C, third reactor outlet: 160°C. After that, the mixture was transferred to the preheater, which had been heated to 220°C, and fed to the vacuum chamber located immediately below the preheater, whose pressure had been adjusted to 8 Torr, to remove the unreacted monomer and the solvent. After that, the resin was cut while being extracted into a strand shape from the vacuum chamber with a gear pump to provide a styrene-based resin composition. While this steady state was kept, resin compositions 24 hr, 72 hr, and 144 hr after the achievement of the steady state were each subjected to evaluations for a molecular weight and a gel-like product. Table 1 shows the results.

[0053] Example 2

A polystyrene resin composition was obtained in the same manner as in Example 1 except that the polyfunctional vinyl copolymer (β) was used in place of the polyfunctional vinyl copolymer (α) in Example 1. Table 1 shows the molecular weights and results of the evaluation for a gel-like product at the respective times.

[0054] Example 3

A polystyrene resin composition was obtained in the same manner as in Example 1 except that the polyfunctional vinyl copolymer (γ) was used in place of the polyfunctional vinyl copolymer (α) in Example 1. Table 1 shows the molecular weights and results of the evaluation for a gel-like product at the respective times.

[0055] Example 4

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 1, 0.06 part by weight, was changed to 0.01 part by weight. Table 1 shows the molecular weights and results of the evaluation for a gel-like product at the respective times.

[0056] Example 5

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that: 70 parts by weight of styrene and 30 parts by weight of ethylbenzene were used; and the addition amount of the polyfunctional vinyl copolymer (α) in Example 1, 0.06 part by weight, was changed to 0.3 part by weight. Table 1 shows the molecular weights and results of the evaluation for a gel-like product at the respective times.

[0057] Example 6

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that: the addition amount of the polyfunctional vinyl copolymer (α) in Example 1, 0.06 part by weight, was changed to 0.1 part by weight; and 0.05 part by weight of t-dodecyl mercaptan (tDM) was added in addition to styrene.

[0058] Comparative Example 1

Linear polystyrene was obtained in the same manner as in Example 1 except that the polyfunctional vinyl copolymer (α) was not added.

[0059] Comparative Example 2

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 1, 0.06 part by weight, was changed to 0.001 part by weight.

[0060] Comparative Example 3

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 1, 0.06 part by weight, was changed to 1 part by weight.

[0061] Comparative Example 4

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that 0.05 part by weight of divinylbenzene was used in place of the polyfunctional vinyl copolymer (α) in Example 1. Table 1 shows the molecular weights and results of the evaluation for a gel-like product at the respective times. At 24 hr, no gel-like product was observed. However, at 72 hr, a gel-like product was generated, and at 144 hr, the polystyrene resin composition was in a state of containing a gel-like product in a large amount.

[0062] Comparative Example 5

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that 0.025 part by weight of divinylbenzene was used in place of the polyfunctional vinyl copolymer (α) in Example 1. At 72 hr, no gel-like product was observed. However, at 144 hr, the generation of a gel-like product was confirmed.

[0063] Comparative Example 6

Apolystyrene resin composition was obtained in the same manner as in Example 1 except that: 0.05 part by weight of divinylbenzene was used in place of the polyfunctional vinyl copolymer (α) in Example 1; and the ratio between styrene and ethylbenzene serving as the solvent was changed to 70 parts by weight of styrene and 30 parts by weight of ethylbenzene.

[0064] Table 1 collectively shows the use amounts of the reaction raw materials and physical properties of the polystyrene resin compositions in Examples 1 to 6 and Comparative Examples 1 to 6.

[0065] Example 7

3 kg of a styrene monomer homogeneously mixed with 0.06 part by weight of the polyfunctional vinyl copolymer (α), and 4 kg of water containing 0.05 part by weight of tricalcium phosphate as a suspension stabilizer and 0.005 part by weight of sodium dodecylbenzenesulfonate as a surfactant were loaded into a reactor having an internal volume of 10 L equipped with a jacket and a stirrer, and the solution was suspended under stirring. To the suspension were added 0.2 part by weight of t-butyl peroxybenzoate as a polymerization initiator and 0.04 part by weight of an α -methylstyrene dimer as a chain transfer agent with respect to 100 parts by weight of the styrene monomer. The stirred suspension was heated at 115°C for 5 hr, and at 140°C for 3 hr to perform polymerization. After the completion of the polymerization, hydrochloric acid was added to the suspension to neutralize the

tricalcium phosphate as the suspension stabilizer. The resultant bead-shaped resin was washed, separated by filtration, and then dried with hot air to provide a styrene-based resin composition.

[0066] Example 8

A styrene-based resin composition was obtained in the same manner as in Example 7 except that the polyfunctional vinyl copolymer (β) was used in place of the polyfunctional vinyl copolymer (α) in Example 7.

[0067] Example 9

A styrene-based resin composition was obtained in the same manner as in Example 7 except that the polyfunctional vinyl copolymer (γ) was used in place of the polyfunctional vinyl copolymer (α) in Example 7.

[0068] Example 10

A polystyrene resin composition was obtained in the same manner as in Example 7 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 7, 0.06 part by weight, was changed to 0.01 part by weight.

[0069] Example 11

A polystyrene resin composition was obtained in the same manner as in Example 7 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 7, 0.06 part by weight, was changed to 0.1 part by weight.

[0070] Comparative Example 7

Linear polystyrene was obtained in the same manner as in Example

7 except that the polyfunctional vinyl copolymer (α) was not added.

[0071] Comparative Example 8

Apolystyrene resin composition was obtained in the same manner as in Example 7 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 7, 0.06 part by weight, was changed to 0.001 part by weight.

[0072] Comparative Example 9

Apolystyrene resin composition was obtained in the same manner as in Example 7 except that the addition amount of the polyfunctional vinyl copolymer (α) in Example 7, 0.06 part by weight, was changed to 1 part by weight.

[0073] Comparative Example 10

Apolystyrene resin composition was obtained in the same manner as in Example 7 except that 0.05 part by weight of divinylbenzene was used in place of the polyfunctional vinyl copolymer (α) in Example 7.

[0074] Table 2 collectively shows the use amounts of the reaction raw materials and physical properties of the polystyrene resin compositions in Examples 7 to 11 and Comparative Examples 7 to 10.

[0075] In Tables 1 to 2, "Crosslinking agent" means the polyfunctional vinyl copolymer or divinylbenzene (DVB), and "Chain transfer agent" means tDM. "Whole Mw" means the weight-average molecular weight of the polystyrene resin composition, "Ratio of Mw of 1,000,000 or more" means a ratio (wt%) in the polystyrene

resin composition, and Y and N in "Evaluation for gel-like product" mean the presence and absence of a gel-like product, respectively.

[0076] [Table 1]

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Crosslinking agent		α	β	γ	α	α	α	None	α	α	DVB	DVB	DVB
Double bond mole fraction(a3)		0.47	0.27	0.14	0.47	0.47	0.47	—	0.47	0.47	2.00	2.00	2.00
Radius of gyration at weight-average molecular weight (nm)		6.4	8.1	10.6	6.4	6.4	6.4	—	6.4	6.4	0.4	0.4	0.4
Ratio between radius of gyration and mole fraction		13.6	30.0	75.7	13.6	13.6	13.6	—	13.6	13.6	0.2	0.2	0.2
Crosslinking agent addition amount (part by weight)		0.06	0.06	0.06	0.01	0.3	0.06	0	0.001	1	0.05	0.025	0.05
Styrene use amount (part by weight)		85	85	85	85	70	85	85	85	85	85	85	70
Solvent use amount (part by weight)		15	15	15	15	30	15	15	15	15	15	15	30
Chain transfer agent (part by weight)		0	0	0	0	0	0.05	0	0	0	0	0	0
Ratio of Mw of 1,000,000 or more (%)		8.8	8.5	9.0	3.9	8.7	7.3	1.4	1.6	—	—	14.5	1.3
Whole Mw (×10 ⁻⁴)	24h	43.9	39.7	45.3	34.9	37.8	33.9	28.7	30.0	—	—	57.2	18.3
	72h	42.9	43.0	43.8	33.5	38.0	36.0	28.2	33.9	—	—	58.6	21.8
	144h	44.8	40.0	44.6	32.9	39.2	35.8	29.8	32.0	—	—	—	21.0
Evaluation for gel-like product (Y/N)	24h	N	N	N	N	N	N	N	N	Y	Y	N	N
	72h	N	N	N	N	N	N	N	N	Y	Y	N	N
	144h	N	N	N	N	N	N	N	N	Y	Y	Y	N

Industrial Applicability

[0078] According to the present invention, it is possible to produce the styrene-based resin composition containing the hyperbranched ultra-high-molecular-weight copolymer and the linear polymer, the styrene-based resin composition being free of any microgel that induces the rupture of a thin-wall portion in processing involving thin-wall drawing typified by foam molding, and being excellent in melting characteristics typified by strain hardening property, thus enabling the production of a uniformly thick-walled product at the time of drawing. Further, the use of the styrene-based resin composition obtained by the present invention in sheet molding suppresses sagging at the time of secondary processing, thickness non-uniformity, and rupture and deterioration of external appearance due to a gel-like product. In addition, the use of the styrene-based resin composition can solve various problems such as drawdown in the case of blow molding, and defoaming, increase in cell size, and generation of open cells in the case of foam molding.

Claims

[Claim 1]

A method of manufacturing a styrene-based resin composition comprising a hyperbranched ultra-high-molecular-weight copolymer and a linear polymer, the method comprising adding, to a monovinyl compound comprising as an essential component styrene, 50 ppm to 5,000 ppm by weight of a solvent-soluble polyfunctional vinyl copolymer having 2 or more vinyl groups per molecule on average and having a branched structure, followed by causing a polymerization reaction to proceed, to obtain a styrene-based resin composition comprising: a hyperbranched ultra-high-molecular-weight copolymer produced through copolymerization of the solvent-soluble polyfunctional vinyl copolymer and the monovinyl compound; and a linear polymer produced through polymerization of the monovinyl compound.

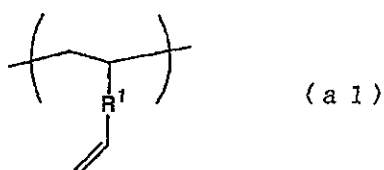
[Claim 2]

A method of manufacturing a styrene-based resin composition according to claim 1, wherein the solvent-soluble polyfunctional vinyl copolymer

is obtained through polymerization of a divinyl compound and a copolymerizable monovinyl compound,

contains a divinyl compound-derived pendant vinyl group-containing unit represented by the following formula (a1) at a mole fraction of from 0.05 to 0.50 in a structural unit, and

has a ratio between a radius of gyration (nm) at a weight-average molecular weight of the solvent-soluble polyfunctional vinyl copolymer and the mole fraction of from 1 to 100:



in the formula, R¹ represents a divinyl compound-derived hydrocarbon group.

[Claim 3]

A styrene-based resin composition, which is obtained by the method according to claim 1 or 2, the styrene-based resin composition comprising:

2.0 to 20.0 wt% of a hyperbranched ultra-high-molecular-weight copolymer having a weight-average molecular weight of 1,000,000 or more; and

80.0 to 98.0 wt% of a linear styrene-based polymer having a weight-average molecular weight of from 100,000 to 500,000,

wherein the styrene-based resin composition has a weight-average molecular weight of from 200,000 to 800,000.