

SPECIFICATION

TITLE OF THE INVENTION

**BLOCK-COPOLYMER-CONTAINING RESIN COMPOSITION
AND MOLDED ARTICLE THEREOF**

TECHNICAL FIELD

[0001] The present invention relates to a resin composition containing a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene. More specifically, the present invention relates to a resin composition containing a block copolymer that is useful as a block-copolymer-containing resin composition by itself or for use by blending with various types of thermoplastic resins, and that provides a molded article, such as a sheet or a film, having excellent impact resistance.

BACKGROUND ART

[0002] Resin compositions containing block copolymers comprising a vinyl aromatic hydrocarbon and a conjugated diene, and having a relatively high vinyl aromatic hydrocarbon content, particularly block copolymers comprising styrene and butadiene, and resin compositions blending said block copolymers with styrenic polymers (GPPS), are widely used in injection molding applications and extrusion molding applications such as sheets and films, due to the fact that molded articles formed therefrom have excellent properties such as impact resistance. Additionally, various proposals have been made for these resin compositions containing block copolymers, in order to further improve the properties such as impact resistance.

Patent Document 1:	JP S52-78260 A
Patent Document 2:	JP H2-59164 B
Patent Document 3:	JP S53-286 A
Patent Document 4:	JP H7-173232 A
Patent Document 5:	JP H5-306313 A
Patent Document 6:	JP H7-228646 A
Patent Document 7:	JP H4-261458 A
Patent Document 8:	JP H11-255851 A
Patent Document 9:	JP 2004-346259 A
Patent Document 10:	WO 2004/085504

SUMMARY OF THE INVENTION

- [0003] The present invention addresses the problem of providing a resin composition containing a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, and a resin composition containing said resin composition and a thermoplastic resin, that are able to provide a molded article such as a sheet or a film that is able to achieve, in particular, a high impact resistance, without any decrease in other properties such as the folding endurance, the tensile modulus or the sheet impact.
- [0004] As a result of carrying out various studies towards achieving a solution to the above-mentioned problem, the present inventors discovered that the above-mentioned problem can be solved by a resin composition wherein (A) the conjugated diene content ratio, (B) the vinyl aromatic hydrocarbon block rate, (C) the Mw/Mn as obtained by gel permeation chromatography (GPC) using a differential refractive index method, and (D) the high-molecular-weight component area ratio in a gel permeation chromatogram are respectively within a specific range, and (E) the loss tangent ($\tan \delta$) as obtained by dynamic viscoelasticity measurements has one maximum value ($\tan \delta$ (max) value) within the temperature range from -100 °C to -60 °C, and the ratio of the $\tan \delta$ value ($\tan \delta$ (max + 30 °C) value) at a temperature 30 °C higher than the temperature at the maximum value ($\tan \delta$ peak temperature) with respect to the $\tan \delta$ value ($\tan \delta$ (max) value) at the maximum value temperature is within a specific range, i.e. ($\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value) is 0.6 or more, thus arriving at the present invention.
- [0005] In particular, the range of 0.6 or more which is the condition relating to the dynamic viscoelasticity in the above-mentioned feature (E) in the resin composition containing a block copolymer according to the present invention is a significant factor in solving the problem addressed by the present invention, as will be explained below.
- [0006] Thus, the present invention relates to a resin composition containing a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, and satisfying the following conditions (A)-(E):
- (A) the content ratio of the conjugated diene is 22 mass% to 35 mass% with respect to the entire block copolymer;
 - (B) the vinyl aromatic hydrocarbon block rate is 98 mass% to 100 mass%;
 - (C) the Mw/Mn (where Mw is the weight-average molecular weight and Mn is the number-average molecular weight) as obtained by gel permeation chromatography (GPC) using the differential refractive index method is 1.3 to 3.5;
 - (D) the area ratio of high-molecular-weight components in a chromatogram obtained by gel permeation chromatography (GPC) using the differential refractive index method is 30% to 55% of the total area; and

(E) the loss tangent ($\tan \delta$) as obtained by dynamic viscoelasticity measurements has one maximum value ($\tan \delta$ (max) value) within the temperature range from $-100\text{ }^{\circ}\text{C}$ to $-60\text{ }^{\circ}\text{C}$, and the $\tan \delta$ value ($\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value) at a temperature $30\text{ }^{\circ}\text{C}$ higher than the temperature at the maximum value ($\tan \delta$ peak temperature) is 0.6 or more with respect to the $\tan \delta$ value ($\tan \delta$ (max) value) at the maximum value temperature.

[0007] By using the block copolymer resin composition comprising a vinyl aromatic hydrocarbon and a conjugated diene or a resin composition containing said resin composition and another thermoplastic resin according to the present invention, it is possible to obtain an extrusion-molded or an injection-molded article such as, for example, a sheet or a film, having a high impact resistance, without any decreases in other properties such as the tensile modulus.

[0008] It is not necessarily clear why the above-mentioned effects are achieved by the present invention. However, it is believed that the effects are achieved due to the resin composition satisfying the above-mentioned conditions (A) to (E), particularly the condition (E) relating to the dynamic viscoelasticity, as will be apparent from the comparison between the examples and the comparative examples indicated below.

[0009] In other words, in the block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene according to the present invention, in order for $\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value/ $\tan \delta$ (max) value to be 0.6 or more, which is the above-mentioned condition (E), it is necessary to repeat soft segment blocks and hard segment blocks. When designing polymers, these two types of blocks are clearly distinguished, but hard segment blocks that lie between soft segment blocks are believed to be incorporated into the soft segment blocks and to appear to function as soft segments. For this reason, it is believed that the content ratio (mass) of conjugated dienes can be reduced, and the rigidity increased, without reducing the proportion of soft segment blocks in a block copolymer. Additionally, it is believed that, since the low-temperature side T_g ($\tan \delta$ peak temperature) remains mostly unchanged as compared with the case in which there are only soft segment blocks, the apparently incorporated hard segment blocks do not inhibit the functions of the soft segments, and good impact resistance is obtained.

MODES FOR CARRYING OUT THE INVENTION

[0010] (Resin Composition)

The resin composition containing a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene according to the present invention (hereinafter referred to simply as “resin composition” or “resin composition according to the present invention”) must satisfy the above-mentioned conditions (A) to (E). Examples of the vinyl aromatic

hydrocarbon that can be used in this case include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, α -methylstyrene, vinylnaphthalene and vinylanthracene. Of these, styrene is preferred. The vinyl aromatic hydrocarbon need not be of just one type, and may be two or more types.

- [0011] Additionally, examples of the conjugated diene include 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene. Of these, 1,3-butadiene or isoprene is preferred. The conjugated diene need not be of just one type, and may be two or more types.
- [0012] The resin composition containing a block copolymer according to the present invention contains a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene. The block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene may be used alone or may be a mixture of two or more types, and may be used in combination with an additive or another resin, within a range not interfering with the effects.
- [0013] The block copolymer of the present invention is preferably of a structure arbitrarily combining blocks comprising vinyl aromatic hydrocarbons and blocks comprising conjugated dienes.
- [0014] In the resin composition, (A) the content ratio of the conjugated diene in the block copolymer must be 22 mass% to 35 mass%. If the conjugated diene content ratio is less than 22 mass%, the impact strength of the resin composition decreases, and this is unfavorable. The conjugated diene content ratio is preferably 23 mass% to 32 mass%, and more preferably 24 mass% to 31 mass%.
- [0015] In the resin composition, (B) the vinyl aromatic hydrocarbon block rate in the resin composition must be 98 mass% to 100 mass%. In this case, the vinyl aromatic hydrocarbon block rate (mass%) is determined as follows.
- Vinyl aromatic hydrocarbon block rate = (amount of vinyl aromatic hydrocarbons present as block-type homopolymer segments in the copolymer/amount of vinyl aromatic hydrocarbons contained in the copolymer) $\times$ 100
- [0016] In the present invention, if the vinyl aromatic hydrocarbon block rate in the resin composition is less than 98%, the impact strength decreases, and this is unfavorable. The block rate is preferably 99 mass% to 100 mass%. In the present invention, for the above-mentioned block rate, the upper limit is 100 mass%, and this value will not be exceeded.
- [0017] In the resin composition, (C) the molecular weight distribution, i.e. the mass-average molecular weight (M_w)/number-average molecular weight (M_n), as obtained by GPC measurements using the differential refractive index method, must be 1.3 to 3.5. If

Mw/Mn is less than 1.3, the impact strength decreases, and this is unfavorable. On the other hand, if Mw/Mn exceeds 3.5, the rigidity decreases, and this is unfavorable. Mw/Mn is preferably from 1.3 to 3.0, and more preferably from 1.4 to 2.5.

[0018] In the resin composition, (D) the area ratio of high-molecular-weight components in a chromatogram obtained by GPC measurements using the differential refractive index method must be 30% to 55% of the total area. If the area ratio of the high-molecular-weight components is less than 30%, the rigidity decreases, and this is unfavorable. On the other hand, if the area ratio exceeds 55%, the impact resistance decreases, and this is unfavorable. The area ratio of the high-molecular-weight components is preferably 30% to 54%, and more preferably 30% to 44%.

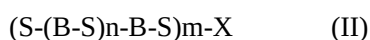
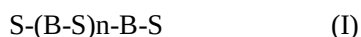
[0019] The area ratio of the high-molecular-weight components in the above-mentioned (D) is determined by identifying the peak having the maximum value for the peak top molecular weight M_p among the peaks having an area ratio within the range of 10% or more with respect to the total peak area in a chromatogram obtained by GPC measurements, and determining the proportional area of that peak with respect to the total peak area.

[0020] Furthermore, in the resin composition, (E) the loss tangent ($\tan \delta$) as obtained by dynamic viscoelasticity measurements must have one maximum value ($\tan \delta$ (max) value) within the temperature range from $-100\text{ }^{\circ}\text{C}$ to $-60\text{ }^{\circ}\text{C}$, and the ratio of the $\tan \delta$ value ($\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value) at a temperature $30\text{ }^{\circ}\text{C}$ higher than the temperature at the maximum value ($\tan \delta$ peak temperature) with respect to the $\tan \delta$ value ($\tan \delta$ (max) value) at the maximum value temperature must be a ratio of 0.6 or more, i.e. ($\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value/ $\tan \delta$ (max) value) must be 0.6 or more.

[0021] In particular, in the present invention, by setting the abovementioned ($\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value/ $\tan \delta$ (max) value) to be preferably 0.65 or more, and more preferably 0.75 or more, the impact resistance and the rigidity of the resulting molded article can be increased in a well-balanced manner, without compromising the other properties. In the present invention, there is no upper limit on the above-mentioned ($\tan \delta$ (max + $30\text{ }^{\circ}\text{C}$) value/ $\tan \delta$ (max) value), and a higher value is more preferable, but the value will normally be less than 1.

[0022] The resin composition preferably contains at least two or more, more preferably three or more block copolymers having different molecular weights, the block copolymers comprising a vinyl aromatic hydrocarbon and a conjugated diene, and satisfying the above-mentioned conditions (A) to (E). These block copolymers preferably have chemical structures represented by the following general formulas (I) and/or (II), and it is preferable to include at least two types, more preferably at least three types, of block copolymers comprising a vinyl aromatic hydrocarbon and a conjugated diene, having different molecular

weights.



[0023] In the above-given general formulas (I) and (II), S denotes a polymer block having vinyl aromatic hydrocarbon monomer units, and B denotes a polymer block having conjugated diene monomer units. m denotes the number of polymer chains bound to a residue of a coupling agent. m is an integer greater than or equal to 1, and is preferably 2 to 10, more preferably 2 to 5. n denotes a number of repeating units and is an integer greater than or equal to 1. For convenience of the polymerization operation, n is preferably 1 to 5, and more preferably 1 to 3. X denotes a residue of a coupling agent. Due to the block copolymers having such a chemical structure, an excellent balance of physical properties such as impact resistance and rigidity is obtained by the resin composition of the present invention.

[0024] The block copolymer having the vinyl aromatic hydrocarbon and conjugated diene block structure represented by the above-indicated general formula (I) and/or the block copolymer having the vinyl aromatic hydrocarbon and conjugated diene block structure represented by general formula (II) can be obtained by anionic polymerization such as that described below.

[0025] In the above-mentioned general formulas (I) and (II), there are no particular limitations on the molecular weights of the S blocks lying between B blocks, but they preferably have a molecular weight of at least 600, more preferably 600 to 20,000. If the molecular weight is 600 or less, the blocks can become indistinguishable from polybutadiene blocks when measuring the block rate, so there is a possibility that the block rate measurement results will be affected. In other words, the boundary between the B blocks and the S blocks must be clearly differentiated, and the degree of polymerization of the S blocks lying between the B blocks is preferably at least 6. Additionally, if the molecular weight exceeds 20,000, the general polystyrene entanglement point molecular weight (Me) will be exceeded, so the hard segment S blocks lying between the soft segment B blocks will not be incorporated into the soft segment B blocks, and the S blocks lying between the B blocks will not be able to be treated as apparent soft segment blocks, and there is a possibility that good physical properties such as impact strength will not be achieved.

[0026] In the present invention, the resin composition preferably contains block copolymers having the vinyl aromatic hydrocarbon and conjugated diene block structure represented by general formula (I) and/or block copolymers having the block structure represented by general formula (II), including all the vinyl aromatic hydrocarbon and conjugated diene block structures represented by the following general formulas (i) to (iii).

In other words, the resin composition is preferably such that the block copolymers represented by the general formula (I) and/or the block copolymers represented by the general formula (II) include block polymers wherein the terminal polystyrene blocks S are of different block chain lengths, such as S1-S2-S3, S2-S3 and S3.

S1-S2-S3-(B-S)_n-B-S4 (i)

S2-S3-(B-S)_n-B-S4 (ii)

S3-(B-S)_n-B-S4 (iii)

[0027] A block copolymer containing all the block structures represented by general formulas (i) to (iii) can be obtained, for example, in a series of anionic polymerization reactions, by adding a polymerization initiator multiple times. When a polymerization initiator is added during a reaction, and thereafter, a monomer is added, a new polymer chain is synthesized, not only at the terminus of the polymer chain that has been polymerized up to that point, but also from the polymerization initiator that was added during the reaction. For this reason, each time a polymerization initiator is added and a monomer is further added, the block structure of a different block chain is formed. For example, by adding a polymerization initiator (e.g., butyllithium or the like) three times during the polymerization, it is possible to obtain a block copolymer containing all of the block structures represented by the above-indicated general formulas (i) to (iii).

[0028] A block copolymer comprising all of the block structures represented by the above-indicated general formulas (i) to (iii) can also be obtained by separately polymerizing, then blending block copolymers respectively having the block copolymers of general formulas (i) to (iii).

[0029] In the above-mentioned general formulas (i) to (iii), S, S1, S2, S3 and S4 are polymer blocks having vinyl aromatic hydrocarbons as monomer units, and B is a polymer block having conjugated dienes as monomer units. n represents the number of repeating units, and is an integer greater than or equal to 1. For convenience of the polymerization operation, n is preferably 1 to 5, and more preferably 1 to 3. Due to the block copolymers having such a chemical structure, an excellent balance of physical properties such as impact resistance and rigidity is obtained by the resin composition of the present invention.

[0030] The resin composition should preferably be such that, during the polymerizations of the above-indicated general formulas (i) to (iii), after all of the used monomers are converted into polymers, in other words, after the production of the S4 blocks in the above-indicated general formulas (i) to (iii), a coupling agent is added before the living active terminals are deactivated with water, alcohol or the like, so as to couple the active terminals. As a result, the balance of physical properties such as impact resistance and rigidity obtained by the resin composition of the present invention will not be affected.

[0031] (Block Copolymer Production Method)

Next, the production of the block copolymer of the present invention will be explained. The block copolymer can be produced by anionic polymerization of a vinyl aromatic hydrocarbon and conjugated diene monomers in an organic solvent, using an organic lithium compound as a polymerization initiator. As the organic solvent, an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane or iso-octane, an alicyclic hydrocarbon such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or ethylcyclohexane, or an aromatic hydrocarbon such as ethylbenzene or xylene may be used. In view of the solubility of the block copolymer, cyclohexane is preferred.

[0032] As the organic lithium compound, a compound having one or more lithium atoms bound to the molecule, for example, a monofunctional organic lithium compound such as ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium or tert-butyllithium, or a polyfunctional organic lithium compound such as hexamethylene dilithium, butadienyl dilithium and isoprenyl dilithium may be used.

[0033] As the vinyl aromatic hydrocarbon and conjugated diene used in the present invention, it is possible to use those mentioned above, of which one or more types of each may be chosen for use in polymerization. Additionally, in living anionic polymerization wherein the aforementioned organic lithium compounds are used as polymerization initiators, almost the entire weight of the vinyl aromatic hydrocarbons and conjugated dienes that are provided for the polymerization reaction are converted to polymers.

[0034] The molecular weight of the block copolymer in the present invention can be controlled by the amount of the polymerization initiator that is added with respect to the entire added amount of the monomer. The block rate of the vinyl aromatic hydrocarbons can be controlled by the supply rate of the vinyl aromatic hydrocarbons and conjugated dienes, and the amount of randomizing agent that is added when polymerizing the vinyl aromatic hydrocarbons and the conjugated dienes to prepare block copolymers.

[0035] A randomizing agent is a compound that functions as a Lewis base during a reaction, and it is possible to use amines, ethers, thioethers and phosphoramides and alkylbenzene sulfonic acid salts, as well as potassium or sodium alkoxides. Examples of amines include tertiary amines such as trimethylamine, triethylamine and tetramethylethylenediamine; and cyclic tertiary amines. Examples of ethers include dimethyl ether, diethyl ether, diphenyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether and tetrahydrofuran (THF). Aside therefrom, it is possible to use triphenylphosphine; hexamethyl phosphoramidate; alkylbenzene potassium or sodium sulfonate; or a butoxide of potassium, sodium, or the like. Preferably, tetrahydrofuran

(THF) is used.

- [0036] The randomizing agent may be of one type or of multiple types. The added concentration is preferably 0.001 parts by mass to 10 parts by mass per 100 parts by mass of the monomers used as the raw material. The time of addition may be before the polymerization reaction starts, or before the polymerization of the copolymer chains. Additional quantities may be added as the need arises.
- [0037] It is also possible to add all of the monomers, and after the reaction has been completed, to add the coupling agent so as to carry out coupling before the living active terminals have been deactivated. In this case, coupling refers to a covalent bond occurring between a living active site positioned at one terminal of a polymer chain and a reaction site in the molecule of the coupling agent, whereby two or more polymer chains bind via a single coupling agent molecule. Additionally, the coupling agent is a compound having, in each molecule, two or more reaction sites that can be attacked by a living active site.
- [0038] Although the coupling agent is not limited, examples include chlorosilane compounds such as dimethyldichlorosilane, silicon tetrachloride and 1,2-bis(methyldichlorosilyl)ethane; alkoxysilane compounds such as dimethyldimethoxysilane, tetramethoxysilane and tetraphenoxysilane; tin tetrachloride; polyhalogenated hydrocarbons; carboxylic acid esters; polyvinyl compounds; and epoxylated oils such as epoxylated soybean oil or epoxylated linseed oil. Epoxylated oils are preferred, and epoxylated soybean oil is more preferred.
- [0039] Examples of difunctional coupling agents having two reaction sites in each molecule include dimethyldichlorosilane, dimethyldimethoxysilane or the like. Examples of trifunctional coupling agents having three reaction sites in each molecule include methyltrichlorosilane and methyltrimethoxysilane. Examples of tetrafunctional coupling agents having four reaction sites in each molecule include tetrachlorosilane, tetramethoxysilane and tetraphenoxysilane. Additionally, epoxylated oils, in addition to having three ester groups in each molecule, have zero to three epoxy groups per long-chain alkyl group on a side having three long-chain alkyl groups, and they are thus polyfunctional coupling agents.
- [0040] The coupling agent may be of one type used alone, or may be a combination of two or more polyfunctional coupling agents. Additionally, it is possible to make combined use of one or more difunctional coupling agents and one or more polyfunctional coupling agents. It is preferable to use one type of polyfunctional coupling agent alone.
- [0041] Additionally, the reaction sites in the coupling agents that can be attacked by living active sites do not necessarily need to react completely, and a portion may remain unreacted. Furthermore, there is no need for a polymer chain having all of the living active sites on one

terminal to react with all of the reaction sites in a coupling agent, and it is acceptable for polymer chains that have remained without reacting to remain on the finally produced block copolymer. Additionally, it is acceptable for there to be, mixed in with the finally produced block copolymers, block copolymers having fewer branches than the number of branches that would be expected if the reaction sites in the used coupling agents were to be completely reacted, and it is also acceptable for there to be, mixed in with the finally produced block copolymers, polymer chains in which the living active sites have simply been replaced with the coupling agent, so that only the coupling agents have bonded to one terminal. In fact, it is conversely preferable, in terms of obtaining good moldability, for the finally produced block copolymers to include two or more of block copolymers having a number of branches equal to the number of branches that would be expected if the reactions sites of the used coupling agent were to be completely reacted, block copolymers having fewer branches than the number of branches that would be expected if the reactions sites of the used coupling agent were to be completely reacted, polymer chains in which the living active sites have been simply replaced with and bonded to the coupling agents, and polymer chains that have remained without reacting with reaction sites on the coupling agents.

[0042] The added amount of the coupling agent is arbitrary, but should preferably be set so that at least a stoichiometric quantity of reaction sites of the coupling agents are present with respect to the living active terminals. Specifically, it is preferable to set the added amount of the coupling agent so that there are one to two equivalent numbers of reaction sites with respect to the number of moles of living active terminals present in the polymerization solution before the coupling step.

[0043] The block copolymer obtained in this way can be inactivated by adding a sufficient quantity of a polymerization terminator such as water, alcohol or carbon dioxide for deactivating the living active terminals. It is possible to use any method for recovering the copolymer from the resulting organic solvent solution of the block copolymer, such as a method of precipitation using a poor solvent such as methanol, a method of precipitation by evaporating the solvent by means of a heating roller or the like (drum-dryer method), a method of concentrating the solution by means of a concentrator, then removing the solvent using a vent-type extruder, and a method of dispersing the solution in water, blowing steam to heat and remove the solvent, and recovering the copolymer (steam stripping method).

[0044] (Blended Resin Composition)

The above-mentioned resin composition may be used in the form of a resin composition that is blended with other thermoplastic resins. Examples of such thermoplastic resins include polystyrene polymers, polyphenylene ether polymers, polyethylene polymers, polypropylene polymers, polybutene polymers, polyvinyl chloride

polymers, polyvinyl acetate polymers, polyamide polymers, thermoplastic polyester polymers, polyacrylate polymers, polyphenoxy polymers, polyphenylene sulfide polymers, polycarbonate polymers, polyacetal polymers, polybutadiene polymers, thermoplastic polyurethane polymers and polysulfine polymers. Examples of preferred thermoplastic resins include polystyrene polymers, general-purpose polystyrenes (GPPS), high-impact polystyrenes (HIPS), methyl methacrylate-styrene copolymers, methacrylate-styrene copolymers, acrylonitrile-styrene copolymers and acrylonitrile-butadiene-styrene copolymers, among which general-purpose polystyrenes (GPPS) are especially preferred.

[0045] While the general-purpose polystyrenes (GPPS) are not defined, they should preferably have a weight-average molecular weight M_w of 180,000 to 400,000, and it is preferable to add 0 to 4 mass% of a liquid paraffin such as white oil.

[0046] The blending mass ratio between the resin composition and the thermoplastic resin of the present invention is preferably block copolymer resin composition/thermoplastic resin = 10/90 to 80/20, more preferably 20/80 to 80/20, even more preferably 30/70 to 70/30, and most preferably 60/40 to 40/60. If the blending mass ratio of the above-mentioned block copolymer composition is less than 10, then the impact strength of the resin composition falls, which is unfavorable, and if the ratio exceeds 80, then the rigidity of the resin composition decreases, which is also unfavorable.

[0047] The above-mentioned resin composition or a resin composition containing said resin composition and a thermoplastic resin may, as needed, further include various types of additives. In other words, if the resin composition is to be subjected to various heat treatments, or if a molded article composed thereof is used in an oxidizing atmosphere or is irradiated by UV rays, an additive such as, for example, a stabilizer, a lubricant, a processing aid, an anti-blocking agent, an anti-static agent, an anti-fogging agent, a weather resistance improving agent, a softening agent, a plasticizing agent, a pigment, a mineral oil, a filler or a flame retardant may be added, in order to prevent the degradation of the physical properties.

[0048] Examples of stabilizers include phenol-based antioxidants such as 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenylacrylate, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenylacrylate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 2,6-di-tert-butyl-4-methylphenol, and phosphorus-based antioxidants such as 2,2-methylenebis(4,6-di-tert-butylphenyl)octylphosphite, trisnonylphenylphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol-diphosphite.

[0049] Additionally, examples of lubricants, processing aids, anti-blocking agents, anti-static agents and anti-fogging agents include saturated fatty acids such as palmitic acid, stearic acid and behenic acid, fatty acid esters such as octyl palmitate and octyl stearate;

pentaerythritol fatty acid esters; fatty acid amides such as erucic acid amide, oleic acid amide, stearic acid amide and behenic acid amide; ethylene bis-stearic acid amide; glycerol mono-fatty acid ester; glycerol di-fatty acid ester; sorbitan fatty acid esters such as sorbitan monopalmitate ester and sorbitan monostearate ester; higher alcohols represented by myristyl alcohol, cetyl alcohol and stearyl alcohol; and high-impact polystyrenes (HIPS).

[0050] Furthermore, examples of weather resistance improving agents include benzotriazole UV absorbing agents such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole; salicylate UV absorbing agents such as 2,4-di-tert-butylphenyl-3',5'-di-tert-butyl-4'-hydroxybenzoate; benzophenone UV absorbing agents such as 2-hydroxy-4-n-octoxybenzophenone; and hindered-amine type weather resistance improving agents such as tetra-cis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate. Furthermore, it is possible to add a liquid paraffin such as white oil or a mineral oil, or a silicone oil or a microcrystalline wax. These additives are preferably used in an amount in the range of 7 mass% or less, more preferably 5 mass% or less, and most preferably 0 to 3 mass% in the resin composition.

[0051] Although there are no particular restrictions on the method of mixing the components when obtaining the resin composition, they may, for example, be dry-blended in a Henschel mixer, a ribbon blender or a V blender, or may be further melted in an extruder and pelletized. Alternatively, they may be added at the time of production of the polymers, before polymerization begins, during the polymerization reaction, or in post-treatment of the polymers or the like.

[0052] (Molded Articles)

The above-mentioned resin compositions may be easily molded, using any conventionally known molding method, such as extrusion molding, injection molding or hollow molding, into products that are useful for an extremely wide variety of practical uses, such as extrusion-molded articles, injection-molded articles, hollow-molded articles, air-pressure-molded articles, vacuum-molded articles and biaxially stretched molded articles, in various shapes including sheets and films.

EXAMPLES

[0053] While the present invention will be explained in further detail by referring to examples below, the present invention should not be construed as being limited by these examples.

[0054] <Polymerization Example 1>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (15).

- (1) 500.0 kg of cyclohexane and 75.0 g of tetrahydrofuran (THF) were loaded into a reaction vessel.
- (2) 780 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 74.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 54 °C.
- (4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.
- (6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 71 °C.
- (8) After the styrene was entirely consumed, 14.7 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 83 °C.
- (9) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 6.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.
- (10) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 14.6 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 84 °C.
- (11) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 6.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 81 °C.
- (12) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 14.7 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 85 °C.
- (13) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 70 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.
- (14) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-(B-S)₂-B-S structure comprising

polystyrene blocks and polybutadiene blocks was obtained. (In the above general formula, S represents a polystyrene block and B represents a polybutadiene block.)

(15) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 1. The peak top molecular weights (Mp) were 399,000/58,000/45,000, the area ratio was 36.2/22.4/41.4 (%), and Mw/Mn was 2.50. The conjugated diene content mass ratio was 22.0%, and the vinyl aromatic hydrocarbon block rate was 100%. The tan δ peak temperature was -78 °C, and tan δ (max + 30 °C) value/tan δ (max) value was 0.84.

The essentials of the above-mentioned Polymerization Example 1 are summarized in Table 1.

[0055] <Polymerization Examples 2-14>

In the above-described Polymerization Example 1, the composition of the block copolymer can be set by adjusting the amounts of the monomers used in the above-mentioned steps (3), (5) and (7)-(13), and the molecular weights can be set by adjusting the amounts of the n-butyllithium used in steps (2), (4) and (6). Therefore, the block copolymer resin compositions of Polymerization Examples 2-14 were obtained by implementing the same procedure as in Polymerization Example 1, aside from the conditions shown in Table 1 below. The essentials of the above-mentioned Polymerization Examples 2-14 are summarized in Table 1.

[0056] <Polymerization Example 15>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (13).

- (1) 500.0 kg of cyclohexane and 75.0 g of THF were loaded into a reaction vessel.
- (2) 780 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 70.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 52 °C.
- (4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.
- (6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic

polymerization. The internal temperature rose to 72 °C.

(8) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 65 °C, and 16.0 kg of 1,3-butadiene and 4.3 kg of styrene were simultaneously added. The internal temperature rose to 79 °C.

(9) After the styrene and the 1,3-butadiene were entirely consumed, the internal temperature of the reaction system was lowered to 65 °C, and 16.0 kg of 1,3-butadiene and 4.4 kg of styrene were simultaneously added. The internal temperature rose to 81 °C.

(10) After the styrene and the 1,3-butadiene were entirely consumed, the internal temperature of the reaction system was lowered to 65 °C, and 16.0 kg of 1,3-butadiene and 4.3 kg of styrene were simultaneously added. The internal temperature rose to 81 °C.

(11) After the styrene and the 1,3-butadiene were entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.

(12) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-T-T-T-S structure comprising polystyrene blocks and tapered blocks of styrene and butadiene was obtained. (In the above general formula, S represents a polystyrene block and T represents a tapered block of styrene and butadiene.)

(13) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 15. The peak top molecular weights (Mp) were 260,000/89,000/77,000, the area ratios was 35.3/22.9/41.8 (%), and Mw/Mn was 1.38. The conjugated diene content mass ratio was 24.0%, and the vinyl aromatic hydrocarbon block rate was 89%. The tan δ peak temperature was -52 °C, and the tan δ (max + 30 °C) value/tan δ (max) value was 0.47.

The essentials of the above-mentioned Polymerization Example 15 are summarized in Table 2.

[0057] <Polymerization Example 16>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (16).

(1) 500.0 kg of cyclohexane and 75.0 g of tetrahydrofuran (THF) were loaded into a reaction vessel.

(2) 1,450 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.

(3) 70.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 53 °C.

(4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane

solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.

(5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.

(6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.

(7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 70 °C.

(8) After the styrene was entirely consumed, 16.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(9) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 6.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(10) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 16.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 85 °C.

(11) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 6.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(12) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 16.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 85 °C.

(13) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 70 °C, 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(14) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, and as a coupling agent, 452 g of epoxylated soybean oil diluted with 3.0 kg of cyclohexane were added, and the polymerization was completed.

(15) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an $(S-(B-S)_2-B-S)_m-X$ structure coupling polymers comprising polystyrene blocks and polybutadiene blocks was obtained. (In the above general formula, S represents a polystyrene block, B represents a polybutadiene block, and X represents a residue of a coupling agent.)

(16) This polymer solution was devolatilized to obtain the block copolymer resin

composition of Polymerization Example 16. The peak top molecular weights (Mp) prior to coupling were 160,000/51,000/41,000, the area ratio was 42.5/19.5/38.0 (%), and Mw/Mn after coupling was 1.67. The conjugated diene content mass ratio was 24.0%, and the vinyl aromatic hydrocarbon block rate was 100%. The $\tan \delta$ peak temperature was -75 °C, and the $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value was 0.82. The essentials of the above-mentioned Polymerization Example 16 are summarized in Table 3.

[0058] <Polymerization Example 17>

A block copolymer comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (12).

- (1) 500.0 kg of cyclohexane and 75.0 g of tetrahydrofuran (THF) were loaded into a reaction vessel.
- (2) 760 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 5.0 kg of styrene was added, the internal temperature was allowed to rise to 80 °C, and the styrene was allowed to undergo anionic polymerization.
- (4) After the styrene was entirely consumed, 3.0 kg of 1,3-butadiene was added and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.
- (5) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 1.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 81 °C.
- (6) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 3.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.
- (7) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 1.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 81 °C.
- (8) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 3.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.
- (9) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 50 °C, 91.8 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 89 °C.
- (10) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 55 °C, 91.8 kg of styrene was added in a single batch, and the polymerization was completed.

(11) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-(B-S)₂-B-S structure comprising polystyrene blocks and polybutadiene blocks was obtained. (In the above general formula, S represents a polystyrene block and B represents a polybutadiene block.)

(12) This polymer solution was devolatilized to obtain the block copolymer of Polymerization Example 17. The peak top molecular weight (Mp) was 386,000, and Mw/Mn was 1.10. The essentials of the above-mentioned Polymerization Example 17 are summarized in Table 4.

[0059] <Polymerization Examples 18 and 19>

In the above-described Polymerization Example 17, the composition of the block copolymer can be set by adjusting the amounts of the monomers used in the above-mentioned steps (3)-(10), and the molecular weights can be set by adjusting the amount of the n-butyllithium used in step (2). Therefore, the block copolymers of Polymerization Examples 18 and 19 were obtained by implementing the same procedure as in Polymerization Example 17, aside from the conditions shown in Table 4 below. The essentials of the above-mentioned Polymerization Examples 18 and 19 are summarized in Table 4.

[0060] <Polymerization Example 20>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (15).

- (1) 500.0 kg of cyclohexane and 75.0 g of THF were loaded into a reaction vessel.
- (2) 890 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 33.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 45 °C.
- (4) After the styrene was entirely consumed, 520 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.
- (6) After the styrene was entirely consumed, 890 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 71 °C.
- (8) After the styrene was entirely consumed, a total of 4.1 kg of styrene and a total of

16.6 kg of 1,3-butadiene were both simultaneously added at a constant addition rate of respectively 25 kg/h and 100 kg/h, while maintaining the internal temperature of the reaction system at 80 °C.

(9) After the styrene and the 1,3-butadiene were entirely consumed, 18.0 kg of styrene was added and the styrene was allowed to undergo anionic polymerization, while maintaining the internal temperature of the reaction system at 80 °C.

(10) After the styrene was entirely consumed, a total of 4.1 kg of styrene and a total of 16.5 kg of 1,3-butadiene were both simultaneously added at a constant addition rate of respectively 25 kg/h and 100 kg/h, while maintaining the internal temperature of the reaction system at 80 °C.

(11) After the styrene and the 1,3-butadiene were entirely consumed, 18.0 kg of styrene was added and the styrene was allowed to undergo anionic polymerization, while maintaining the internal temperature of the reaction system at 80 °C.

(12) After the styrene was entirely consumed, a total of 4.1 kg of styrene and a total of 16.6 kg of 1,3-butadiene were both simultaneously added at a constant addition rate of respectively 25 kg/h and 100 kg/h, while maintaining the internal temperature of the reaction system at 80 °C.

(13) After the styrene and the 1,3-butadiene were entirely consumed, the temperature of the reaction system was lowered to 75 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.

(14) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-(R-S)₂-R-S structure comprising polystyrene blocks and random blocks of styrene and butadiene was obtained. (In the above general formula, S represents a polystyrene block and R represents a random block of styrene and butadiene.)

(15) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 20. The peak top molecular weights (Mp) were 191,000/123,000/107,000, the area ratio was 32.6/20.8/46.6 (%), and Mw/Mn was 1.30. The conjugated diene content mass ratio was 24.9%, and the vinyl aromatic hydrocarbon block rate was 95%. The tan δ peak temperature was -65 °C, and the tan δ (max + 30 °C) value/tan δ (max) value was 0.74. The essentials of the above-mentioned Polymerization Example 20 are summarized in Table 5.

[0061] <Polymerization Example 21>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (11).

(1) 500.0 kg of cyclohexane and 75.0 g of THF were loaded into a reaction vessel.

- (2) 780 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 70.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 52 °C.
- (4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.
- (6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 72 °C.
- (8) After the styrene was entirely consumed, a total of 12.2 kg of styrene and a total of 48.8 kg of 1,3-butadiene were both simultaneously added at a constant addition rate of respectively 25 kg/h and 100 kg/h, while maintaining the internal temperature of the reaction system at 80 °C.
- (9) After the styrene and the 1,3-butadiene were entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.
- (10) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-R-S structure comprising polystyrene blocks and random blocks of styrene and butadiene was obtained. (In the above general formula, S represents a polystyrene block and R represents a random block of styrene and butadiene.)
- (11) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 21. The peak top molecular weights (Mp) were 283,000/91,000/78,000, the area ratio was 39.2/18.8/42.0 (%), and Mw/Mn was 1.52. The conjugated diene content mass ratio was 24.4%, and the vinyl aromatic hydrocarbon block rate was 95%. The tan δ peak temperature was -65 °C, and tan δ (max + 30 °C) value/tan δ (max) value was 0.47.

The essentials of the above-mentioned Polymerization Example 21 are summarized in Table 6.

[0062] <Polymerization Examples 22 and 23>

In the above-described Polymerization Example 21, the composition of the block

copolymer can be set by adjusting the amounts of the monomers used in the above-mentioned steps (3), (5) and (7)-(9), and the molecular weights can be set by adjusting the amount of the n-butyllithium used in steps (2), (4) and (6). Therefore, the block copolymers of Polymerization Examples 22 and 23 were obtained by implementing the same procedure as in Polymerization Example 21, aside from the conditions shown in Table 6 below. Polymerization Examples 22 and 23 were block copolymers having S-B-S structures comprising polystyrene blocks and polybutadiene blocks. In the above-described formula, S represents a polystyrene block and B represents a polybutadiene block. The essentials of the above-mentioned Polymerization Examples 22 and 23 are summarized in Table 6.

[0063] <Polymerization Example 24>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (13).

- (1) 500.0 kg of cyclohexane and 75.0 g of tetrahydrofuran (THF) were loaded into a reaction vessel.
- (2) 780 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.
- (3) 70.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 51 °C.
- (4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.
- (6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.
- (7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 71 °C.
- (8) After the styrene was entirely consumed, 24.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 86 °C.
- (9) After the 1,3-butadiene was entirely consumed, the internal temperature was lowered to 80 °C, 13.0 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 85 °C.
- (10) After the styrene was entirely consumed, the internal temperature of the reaction

system was lowered to 75 °C, 24.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 88 °C.

(11) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 70 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.

(12) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-(B-S)₁-B-S structure comprising polystyrene blocks and polybutadiene blocks was obtained. (In the above general formula, S represents a polystyrene block and B represents a polybutadiene block.)

(13) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 24. The peak top molecular weights (Mp) were 394,000/56,000/49,000, the area ratio was 35.2/22.5/42.3 (%), and Mw/Mn was 2.16. The conjugated diene content mass ratio was 24.0%, and the vinyl aromatic hydrocarbon block rate was 100%. The tan δ peak temperature was -75 °C, and the tan δ (max + 30 °C) value/tan δ (max) value was 0.79. The essentials of the above-mentioned Polymerization Example 24 are summarized in Table 7.

[0064] <Polymerization Example 25>

A block copolymer resin composition comprising styrene and 1,3-butadiene was produced by means of the following operations (1) to (17).

(1) 500.0 kg of cyclohexane and 75.0 g of tetrahydrofuran (THF) were loaded into a reaction vessel.

(2) 780 mL of a 10 mass% cyclohexane solution of n-butyllithium was added thereto as a polymerization initiator solution and the internal temperature was held at 30 °C.

(3) 70.8 kg of styrene was added and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 52 °C.

(4) After the styrene was entirely consumed, 790 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.

(5) 15.2 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 64 °C.

(6) After the styrene was entirely consumed, 1,580 mL of a 10 mass% cyclohexane solution of n-butyllithium was added as a polymerization initiator solution and the internal temperature was held at 60 °C.

(7) 26.5 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 71 °C.

(8) After the styrene was entirely consumed, 12.0 kg of 1,3-butadiene was added, and

the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 81 °C.

(9) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 4.3 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 81 °C.

(10) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 12.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 83 °C.

(11) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 4.4 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(12) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 12.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 83 °C.

(13) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 80 °C, 4.3 kg of styrene was added, and the styrene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(14) After the styrene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 12.0 kg of 1,3-butadiene was added, and the 1,3-butadiene was allowed to undergo anionic polymerization. The internal temperature rose to 82 °C.

(15) After the 1,3-butadiene was entirely consumed, the internal temperature of the reaction system was lowered to 75 °C, 26.5 kg of styrene was added in a single batch, and the polymerization was completed.

(16) Finally, all of the polymerization active terminals were deactivated with water, and a polymer solution containing a polymer having an S-(B-S)₃-B-S structure comprising polystyrene blocks and polybutadiene blocks was obtained. (In the above general formula, S represents a polystyrene block and B represents a polybutadiene block.)

(17) This polymer solution was devolatilized to obtain the block copolymer resin composition of Polymerization Example 25. The peak top molecular weights (Mp) were 317,000/61,000/47,000, the area ratio was 35.8/20.9/43.3 (%), and Mw/Mn was 2.08. The conjugated diene content mass ratio was 24.0%, and the vinyl aromatic hydrocarbon block rate was 100%. The tan δ peak temperature was -72 °C, and tan δ (max + 30 °C) value/tan δ (max) value was 0.88. The essentials of the above-mentioned Polymerization Example 25 are summarized in Table 8.

[0065] <Blend Examples>

<Blend Example 1>

A block copolymer resin composition was produced by mixing together the block copolymers obtained in Polymerization Examples 17-19 at the blending ratios (mass%) shown in Table 9. The block copolymer resin composition was melt-kneaded using a single-screw extruder (manufactured by Tabata Industrial Machinery, HV-40-30, ϕ 40 mm) at an extrusion temperature of 200 °C and a screw rotation speed of 100 rpm, extruded in strands, cooled, then pelletized in a pelletizer. The blending composition, the peak top molecular weights (Mp), the surface area ratio and Mw/Mn of the block copolymer resin composition in Blend Example 1, and the conjugated diene content mass ratio, the vinyl aromatic hydrocarbon block rate, the $\tan \delta$ peak temperature and the $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value of the block copolymer resin composition are all shown in Table 9.

[0066] <Measurement of molecular weight and dispersity Mw/Mn>

A gel permeation chromatograph (GPC) was used. In the present invention, when not particularly noted, the molecular weight refers to the peak top molecular weight Mp, and when coupling is implemented, it refers to the Mp prior to coupling. Additionally, the dispersity is the weight-average molecular weight Mw/number-average molecular weight Mn, and when coupling is implemented, it refers to the Mw/Mn after coupling.

GPC device name: "HLC-8220GPC" manufactured by Tosoh

Columns used: Four serially connected "Shodex GPCKF-404" columns, manufactured by Showa Denko; column temperature: 40 °C; detection method: differential refractive index method; mobile phase: tetrahydrofuran

Sample concentration: 2 mass%

Calibration curves: Prepared using standard polystyrenes manufactured by Varian (peak top molecular weights Mp = 2,560,000; 841,700; 280,500; 143,400; 63,350; 31,420; 9,920; 2,930)

[0067] <Conjugated diene content ratio (mass) of resin composition>

The conjugated diene content ratios of the block copolymer resin compositions were respectively calculated from the blending ratios and the proportional amount of 1,3-butadiene used with respect to the amount of all the monomers used in the above-described polymerization examples.

[0068] <Styrene block rate in resin composition>

Calculated by using nuclear magnetic resonance (NMR) to measure ^1H -NMR. The block styrene amount W was obtained by determining the integral of the peak intensity from 6.2 to 6.8 ppm, attributed to the two protons added at the ortho positions among the five protons added to the aromatic ring of a polystyrene, and converting the value to five protons.

Additionally, the total styrene amount (total vinyl aromatic hydrocarbon amount) W0 was obtained by determining the integral of the peak intensity from 6.2 to 7.6 ppm,

including the integral of the peak intensity from 6.8 to 7.6 ppm, attributed to the three protons added at the para and meta positions, and dividing the value by the integral of the peak intensity of deuteriochloroform.

The block rate was calculated by substituting W and W0 into the below-indicated defining formula. The block styrene amount (block vinyl aromatic hydrocarbon amount) W was measured for chains having five or more monomer units, because of the sensitivity of the device.

$$\text{Styrene block rate (\%)} = (W/W_0) \times 100$$

Nuclear magnetic resonance device name: AVANCE-300 manufactured by Bruker Biospin

Measured nuclear species: ^1H ; resonance frequency: 300 MHz (^1H); measurement solvent: CDCl_3

[0069] <tan δ peak temperature and tan δ (max + 30 °C) value/tan δ (max) value>

These were determined using dynamic viscoelasticity measurements (charts). The measurements were used to determine the loss tangent (tan δ), and among the peak values of tan δ in the temperature range from -100 ° to -60 °C, the highest value was defined as the “tan δ (max) value” and the temperature thereof was defined as the “tan δ peak temperature”. Next, the tan δ value at a temperature 30 °C higher than the tan δ peak temperature was defined as the “tan δ (max + 30 °C) value”, and tan δ (max + 30 °C) value/tan δ (max) value was calculated.

[0070] <Dynamic viscoelasticity measurement>

Using the below-indicated device, the storage elasticity (E'), the loss elasticity (E'') and the loss tangent (tan δ) were measured (note that tan $\delta = E''/E'$) while applying strain and stress to the test samples in a tensile direction at a frequency of 1 Hz and raising the temperature at a rate of 4 °C/min. The samples of the resin compositions for use in measuring the dynamic viscoelasticity were held under pressure for 2 minutes at conditions of 200 °C to 220 °C using a hot press in order to relieve their orientation, then rapidly cooled to form unoriented 0.6 mm-thick sheets. Thereafter, the sheets were stored for at least 24 hours in a room controlled to a temperature of 23 °C and a relative humidity of 50% RH, and then used.

Dynamic viscoelasticity measurement device: RSA3 manufactured by TA Instruments

Set temperature range: -120 to 130 °C; set temperature increase rate: 4 °C/min

Measurement frequency: 1 Hz

[0071] According to Polymerization Examples 2 and 23, the conjugated diene mass ratio was able to be reduced by 6.5% without changing the block rate or the tan δ peak

temperature, by repeating polybutadiene blocks and polystyrene blocks. In this case, $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value was found to be 0.6 or more.

[0072] On the other hand, according to Polymerization Examples 2 and 21, when the conjugated diene mass ratios of the block copolymer resin compositions were held constant, and polybutadiene blocks and polystyrene blocks were repeated (Polymerization Example 2), and when repetition was not implemented and the styrene/1,3-butadiene ratio was changed for random blocks (Polymerization Example 21), the block rate, the $\tan \delta$ peak temperature, and $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value were found to change.

[0073] Additionally, according to Polymerization Examples 8 and 20, when polybutadiene blocks and polystyrene blocks were repeated (Polymerization Example 8), and when random blocks and polystyrene blocks were repeated (Polymerization Example 20), the block rate and the $\tan \delta$ peak temperature changed, but $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value was at least 0.6 in both cases. In other words, the repetition of soft segments and hard segments was found to result in $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value being 0.6 or more.

[0074] According to Polymerization Examples 2 and 15, when the conjugated diene mass ratios of the block copolymer resin compositions were held constant, and polybutadiene blocks and polystyrene blocks were repeated (Polymerization Example 2), and when tapered blocks were repeated (Polymerization Example 15), the block rate, the $\tan \delta$ peak temperature, and $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value were found to change.

[0075] <Examples 1-16 and Comparative Examples 1-11>

· Preparation of GPPS Blend Sheet

The block copolymer resin compositions and GPPS were mixed at the blending ratios (mass%) shown in Tables 10 and 11, and sheets were molded using the following procedures. Using a $\phi 40$ mm single-screw extruder VS40-26, manufactured by Tanabe Plastics, equipped with a T-die having a width of 40 cm on the tip thereof, sheet extrusion was performed using the resins of the blend examples, with the extrusion temperature set to 200 °C, the T-die temperature set to 200 °C and the screw rotation speed set to 60 rpm, and single-layer sheets having a sheet thickness of 0.6 mm were produced using a 480-type sheeting device manufactured by Tanabe Plastics, with the cooling roll temperature set to 50 °C. The thicknesses of the sheets were adjusted by the openness of the die lips, and the sheet withdrawal rate was held constant. The resins that were used are shown in Tables 10 and 11. As the GPPS, a general-purpose polystyrene resin (Toyostyrol GP G200C, manufactured by Toyo Styrene, having a peak top molecular weight (Mp) of 286,000 and Mw/Mn of 2.53) was used.

[0076] <Sheet Impact>

An impact tester (manufactured by Tester Sangyo) was used to make measurements

using a hammer core having a tip with a diameter of 12.7 mm. The other measurement conditions were in accordance with ASTM D3420. A value of “>5.0” was recorded when punch-through did not occur.

[0077] <Dupont impact strength>

Using a Dupont impact tester (manufactured by Toyoseiki), twenty 60-mm-square test pieces, cut out from a sheet, were placed on a receiving stand, a hammer core having a tip with a diameter of 6.35 mm was placed on each test piece, and a 100 g weight was dropped onto the upper end of the hammer core, after which the test pieces were visually investigated for the presence or absence of cracks occurring on the sheets, and energy values were determined by conversion. Using two or three other preliminary test pieces prior to the main measurements, the approximate weight-dropping height at which the sheets were expected to break was determined. The first piece was measured at the weight-dropping height determined from the preliminary measurement results, and the second and subsequent pieces were similarly measured on the basis of the previous measurement results, except that the weight-dropping height was raised by 5 cm if the sheet did not crack, and the weight-dropping height was lowered by 5 cm if the sheet did crack. This operation was consecutively performed 20 times, and based on the records for the weight-dropping heights and the presence or absence of cracks each time, the Dupont impact strength was determined using the formulas indicated below. When no cracks occurred, a value of “> 0.90” was recorded.

$X = \text{sum of (height} \times \text{number of sheets A) / number (m) of sheets A}$ where A indicates sheets that did not crack

$Y = \text{sum of (height} \times \text{number of sheets B) / number (m) of sheets B}$ where B indicates sheets that cracked

$$Z = (X + Y) / 2(m)$$

$$\text{Dupont impact strength (J)} = 0.1 \text{ (kg)} \times 9.8 \text{ (m/s}^2\text{)} \times Z(m)$$

[0078] <Folding endurance>

An MIT folding fatigue tester (manufactured by Toyoseiki, MIT-DA) was used the measure samples cut to MD direction × TD direction = 100 mm × 10 mm and 10 mm × 100 mm, each sample being measured six times, and their average value was used. The measurements were made at a folding angle of 45° to left and right, folding rate 175 times/min, and with a load of 1 kg. When the measurement average exceeded 1,000 times, a value of “> 1000” was recorded.

[0079] <Tensile elasticity>

Using a tensilon universal tester (manufactured by A and D Company, RTC-1210A), a dumbbell-type test piece in compliance with JIS K6732 was cut from a sheet so as to have

the long side aligned with the MD direction, and the tensile elasticity (rigidity) in the MD direction was measured at an initial chuck spacing of 50 mm, a pulling rate of 10 mm/min and in a 23 °C environment.

- [0080] According to Examples 1 and 3, and Comparative Examples 1 and 2, when the conjugated diene content ratio in the resin composition was less than 22%, the impact strength was low, and when it exceeded 35%, the rigidity decreased.
- [0081] According to Example 2 and Comparative Examples 3, 9 and 10, when the vinyl aromatic hydrocarbon block rate in the resin composition was less than 98%, the impact strength decreased.
- [0082] According to Examples 4 and 5 and Comparative Examples 4 and 5, when M_w/M_n , which is the molecular weight distribution in the resin composition, was less than 1.3, the impact strength was low, and when it exceeded 3.5, the rigidity decreased.
- [0083] According to Examples 6 and 7 and Comparative Examples 6 and 7, when the area ratio of the high-molecular-weight components was less than 30%, the rigidity was low, and when it exceeded 55%, the impact strength decreased.
- [0084] According to Example 2 and Comparative Examples 9 and 10, when the conjugated diene mass ratios of the block copolymer resin compositions were held constant, the impact strength decreased if the “ $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value” was less than 0.6. According to Example 2 and Comparative Example 11, when the vinyl aromatic hydrocarbon block rates of the block copolymer resin compositions were held constant, the rigidity decreased if the “ $\tan \delta$ (max + 30 °C) value/ $\tan \delta$ (max) value” was less than 0.6.
- [0085] According to Examples 2 and 9, the physical properties are not affected by whether or not the block copolymers in the resin composition have undergone coupling. According to Examples 2 and 10, the physical properties are not affected, whether the block copolymers in the resin compositions are simultaneously polymerized in a reaction vessel, or separately polymerized and blended afterwards.
- [0086] According to Examples 2 and 6 and Comparative Examples 8 and 11, by repeating the polybutadiene blocks and the polystyrene blocks in a block copolymer in a resin composition, the conjugated diene mass ratio was reduced and the rigidity was increased without compromising the impact strength. It is believed that the polystyrene blocks sandwiched between polybutadiene blocks appeared to be incorporated into the polybutadiene blocks so as to function as soft segments, and the low-temperature-side T_g ($\tan \delta$ peak temperature) did not change, so the soft segment functions were not inhibited, as a result of which the impact resistance was raised.
- [0087] According to Example 8 and Comparative Example 3, when comparing the case in which the soft segments in the block copolymers in the resin composition are repeating

polybutadiene blocks and polystyrene blocks with the case in which they are repeating random blocks and polystyrene blocks, the impact strength was lower in the latter case. In other words, the soft segments of the block copolymers in the resin compositions must be polybutadiene blocks.

[0088] According to Example 2 and Comparative Example 10, when the case in which polybutadiene blocks and polystyrene blocks are repeated was compared with the case in which tapered blocks were repeated while holding the conjugated diene mass ratios of the block copolymer resin compositions constant, the impact strength was lower in the latter case. In other words, when polybutadiene blocks and polystyrene blocks are repeated, it appears that the boundary therebetween must be clearly distinguished.

[0089] [Table 1]

Polymerization Example No.			1	2	3	4	5	6	7	8	9	10	11	12	13	14	
(1)	Cyclohexane	kg	500	500	500	500	500	500	500	500	500	500	500	500	500	500	
	THF	g	75	75	75	75	75	75	75	75	75	75	75	75	75	75	
(2)	n-Butyllithium	ml	780	780	1000	1300	610	780	1200	800	780	1000	1300	590	610	1400	
(3)	Styrene	kg	74.8	70.8	48.8	70.8	70.8	56.8	70.8	33.8	76.8	46.8	70.8	70.8	56.8	70.8	
(4)	n-Butyllithium	ml	790	790	440	400	780	780	400	520	790	440	200	780	780	400	
(5)	Styrene	kg	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	
(6)	n-Butyllithium	ml	1580	1580	1020	900	1580	1220	590	890	1580	1020	600	1700	1220	590	
(7)	Styrene	kg	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	
(8)	1,3-Butadiene	kg	14.7	16.0	23.3	16.0	16.0	20.7	16.0	20.7	14.0	24.0	16.0	16.0	20.7	16.0	
(9)	Styrene	kg	6.5	6.5	6.5	6.5	6.5	6.5	6.5	18.0	6.5	6.5	6.5	6.5	6.5	6.5	
(10)	1,3-Butadiene	kg	14.6	16.0	23.4	16.0	16.0	20.6	16.0	20.6	14.0	24.0	16.0	16.0	20.6	16.0	
(11)	Styrene	kg	6.5	6.5	6.5	6.5	6.5	6.5	6.5	18.0	6.5	6.5	6.5	6.5	6.5	6.5	
(12)	1,3-Butadiene	kg	14.7	16.0	23.3	16.0	16.0	20.7	16.0	20.7	14.0	24.0	16.0	16.0	20.7	16.0	
(13)	Styrene	kg	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	
(15)	High Mol. Wt.	Mp × 10 ⁻⁴	-	39.9	39.4	28.9	19.7	83.0	41.0	23.7	23.0	29.3	24.3	23.9	96.6	77.1	21.6
		Area ratio	%	36.2	43.7	30.1	49.3	32.3	30.0	55.0	32.0	40.6	31.2	55.0	31.6	26.0	58.4
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	5.8	5.6	10.9	8.1	8.4	10.2	11.2	12.8	6.1	10.6	12.3	8.2	11.4	10.9
		Area ratio	%	22.4	19.9	21.5	15.7	15.8	18.2	15.1	18.0	19.1	20.7	12.1	15.4	18.3	12.6
		Mp × 10 ⁻⁴	-	4.5	4.9	8.9	6.7	5.7	7.8	9.5	10.6	4.7	8.8	10.3	5.4	8.3	9.3
		Area ratio	%	41.4	36.4	48.4	35.0	51.9	51.8	29.9	50.0	40.3	48.1	32.9	53.0	55.7	29.0
	Mw/Mn		-	2.50	2.48	1.38	1.34	3.50	1.70	1.36	1.34	2.00	1.35	1.24	4.05	2.50	1.30
Conjugated diene mass ratio		%	22.0	24.0	35.0	24.0	24.0	31.0	24.0	31.0	21.0	36.0	24.0	24.0	31.0	24.0	
Block rate		%	100	100	98	100	100	99	100	99	100	100	100	100	100	100	
tan δ peak temperature		°C	-78	-74	-72	-75	-74	-72	-74	-72	-80	-69	-75	-71	-70	-76	
tan δ (max + 30 °C) / tan δ (max)		-	0.84	0.85	0.80	0.65	0.75	0.86	0.65	0.84	0.78	0.83	0.65	0.80	0.86	0.64	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0090] [Table 2]

Polymerization Example No.			15	
(1)	Cyclohexane	kg	500	
	THF	g	75	
(2)	n-Butyllithium	ml	780	
(3)	Styrene	kg	70.8	
(4)	n-Butyllithium	ml	790	
(5)	Styrene	kg	15.2	
(6)	n-Butyllithium	ml	1580	
(7)	Styrene	kg	26.5	
(8)	1,3-Butadiene	kg	16.0	
	Styrene	kg	4.3	
(9)	1,3-Butadiene	kg	16.0	
	Styrene	kg	4.4	
(10)	1,3-Butadiene	kg	16.0	
	Styrene	kg	4.3	
(11)	Styrene	kg	26.5	
(13)	High Mol. Wt.	Mp × 10 ⁻⁴	-	26.0
		Area ratio	%	35.3
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	8.9
		Area ratio	%	22.9
		Mp × 10 ⁻⁴	-	7.7
		Area ratio	%	41.8
	Mw/Mn		-	1.38
Conjugated diene mass ratio		%	24.0	
Block rate		%	89	
tan δ peak temperature		°C	-52	
tan δ (max + 30 °C) / tan δ (max)		-	0.47	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0091] [Table 3]

Polymerization Example No.			16	
(1)	Cyclohexane	kg	500	
	THF	g	75	
(2)	n-Butyllithium	ml	1450	
(3)	Styrene	kg	70.8	
(4)	n-Butyllithium	ml	790	
(5)	Styrene	kg	15.2	
(6)	n-Butyllithium	ml	1580	
(7)	Styrene	kg	26.5	
(8)	1,3-Butadiene	kg	16.0	
(9)	Styrene	kg	6.5	
(10)	1,3-Butadiene	kg	16.0	
(11)	Styrene	kg	6.5	
(12)	1,3-Butadiene	kg	16.0	
(13)	Styrene	kg	26.5	
(14)	Epoxylated soybean oil	g	452	
	Cyclohexane	kg	3.0	
(16)	High Mol. Wt.	Mp × 10 ⁻⁴	-	16.0
		Area ratio	%	42.5
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	5.1
		Area ratio	%	19.5
		Mp × 10 ⁻⁴	-	4.1
		Area ratio	%	38.0
	Mw/Mn		-	1.67
Conjugated diene mass ratio		%	24.0	
Block rate		%	100	
tan δ peak temperature		°C	-75	
tan δ (max + 30 °C) / tan δ (max)		-	0.82	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0092] [Table 4]

Polymerization Example No.			17	18	19
(1)	Cyclohexane	kg	500	500	500
	THF	g	75	75	75
(2)	n-Butyllithium	ml	760	4360	5070
(3)	Styrene	kg	5.0	38.8	46.5
(4)	1,3-Butadiene	ml	3.0	23.5	28.1
(5)	Styrene	kg	1.2	9.5	11.4
(6)	1,3-Butadiene	ml	3.0	23.4	28.0
(7)	Styrene	kg	1.2	9.5	11.4
(8)	1,3-Butadiene	kg	3.0	23.5	28.1
(9)	Styrene	kg	91.8	71.8	46.5
(10)	Styrene	kg	91.8	-	-
(12)	$M_p \times 10^{-4}$	-	38.6	5.5	4.9
	Mw/Mn	-	1.10	1.08	1.12
Conjugated diene mass ratio		%	4.5	35.2	42.1

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0093] [Table 5]

Polymerization Example No.				20
(1)	Cyclohexane		kg	500
	THF		g	75
(2)	n-Butyllithium		ml	890
(3)	Styrene		kg	33.8
(4)	n-Butyllithium		ml	520
(5)	Styrene		kg	15.2
(6)	n-Butyllithium		ml	890
(7)	Styrene		kg	26.5
(8)	Styrene		kg	4.1
	Addition rate		kg/h	25
	1,3-Butadiene		kg	16.6
	Addition rate		kg/h	100
(9)	Styrene		kg	18.0
(10)	Styrene		kg	4.1
	Addition rate		kg/h	25
	1,3-Butadiene		kg	16.5
	Addition rate		kg/h	100
(11)	Styrene		kg	18.0
(12)	Styrene		kg	4.1
	Addition rate		kg/h	25
	1,3-Butadiene		kg	16.6
	Addition rate		kg/h	100
(13)	Styrene		kg	26.5
(15)	High Mol. Wt.	Mp × 10 ⁻⁴	-	19.1
		Area ratio	%	32.6
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	12.3
		Area ratio	%	20.8
		Mp × 10 ⁻⁴	-	10.7
		Area ratio	%	46.6
	Mw/Mn		-	1.30
Conjugated diene mass ratio			%	24.9
Block rate			%	95
tan δ peak temperature			°C	-65
tan δ (max + 30 °C) / tan δ (max)			-	0.74

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0094] [Table 6]

Polymerization Example No.			21	22	23	
(1)	Cyclohexane	kg	500	500	500	
	THF	g	75	75	75	
(2)	n-Butyllithium	ml	780	780	780	
(3)	Styrene	kg	70.8	56.8	70.8	
(4)	n-Butyllithium	ml	790	790	790	
(5)	Styrene	kg	15.2	15.2	15.2	
(6)	n-Butyllithium	ml	1580	1220	1580	
(7)	Styrene	kg	26.5	26.5	26.5	
(8)	Styrene	kg	12.2	-	-	
	Addition rate	kg	25	-	-	
	1,3-Butadiene	kg	48.8	75.0	61.0	
	Addition rate	kg	100	-	-	
(9)	Styrene	kg	26.5	26.5	26.5	
(11)	High Mol. Wt.	Mp × 10 ⁻⁴	-	28.3	34.4	24.5
		Area ratio	%	39.2	30.3	48.6
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	9.1	9.7	6.4
		Area ratio	%	18.8	26.0	12.7
		Mp × 10 ⁻⁴	-	7.8	8.2	5.2
		Area ratio	%	42.0	43.7	38.7
	Mw/Mn		-	1.52	1.61	1.73
	Conjugated diene mass ratio		%	24.4	37.5	30.5
Block rate		%	95	100	100	
tan δ peak temperature		°C	-65	-75	-76	
tan δ (max + 30 °C) / tan δ (max)		-	0.47	0.64	0.45	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0095] [Table 7]

Polymerization Example No.			24	
(1)	Cyclohexane	kg	500	
	THF	g	75	
(2)	n-Butyllithium	ml	780	
(3)	Styrene	kg	70.8	
(4)	n-Butyllithium	ml	790	
(5)	Styrene	kg	15.2	
(6)	n-Butyllithium	ml	1580	
(7)	Styrene	kg	26.5	
(8)	1,3-Butadiene	kg	24.0	
(9)	Styrene	kg	13.0	
(10)	1,3-Butadiene	kg	24.0	
(11)	Styrene	kg	26.5	
(13)	High Mol. Wt.	Mp $\times 10^{-4}$	-	39.4
		Area ratio	%	35.2
	Low Mol. Wt.	Mp $\times 10^{-4}$	-	5.6
		Area ratio	%	22.5
		Mp $\times 10^{-4}$	-	4.9
		Area ratio	%	42.3
	Mw/Mn		-	2.16
Conjugated diene mass ratio		%	24.0	
Block rate		%	100	
tan δ peak temperature		°C	-75	
tan δ (max + 30 °C) / tan δ (max)		-	0.79	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0096] [Table 8]

Polymerization Example No.			25	
(1)	Cyclohexane	kg	500	
	THF	g	75	
(2)	n-Butyllithium	ml	780	
(3)	Styrene	kg	70.8	
(4)	n-Butyllithium	ml	790	
(5)	Styrene	kg	15.2	
(6)	n-Butyllithium	ml	1580	
(7)	Styrene	kg	26.5	
(8)	1,3-Butadiene	kg	12.0	
(9)	Styrene	kg	4.3	
(10)	1,3-Butadiene	kg	12.0	
(11)	Styrene	kg	4.4	
(12)	1,3-Butadiene	kg	12.0	
(13)	Styrene	kg	4.3	
(14)	1,3-Butadiene	kg	12.0	
(15)	Styrene	kg	26.5	
(17)	High Mol. Wt.	Mp × 10 ⁻⁴	-	31.7
		Area ratio	%	35.8
	Low Mol. Wt.	Mp × 10 ⁻⁴	-	6.1
		Area ratio	%	20.9
		Mp × 10 ⁻⁴	-	4.7
		Area ratio	%	43.3
	Mw/Mn		-	2.08
Conjugated diene mass ratio		%	24.0	
Block rate		%	100	
tan δ peak temperature		°C	-72	
tan δ (max + 30 °C) / tan δ (max)		-	0.88	

For n-butyllithium, the amount of 10 mass% cyclohexane solution added.

Mp: peak top molecular weight; Mn: number-average molecular weight; Mw: weight-average molecular weight

[0097] [Table 9]

				Blend Ex 1
Resin Composition Blend	Poly Ex 17		%	44.4
	Poly Ex 18		%	20.0
	Poly Ex 19		%	35.6
GPC	High Mol. Wt.	Mp $\times 10^{-4}$	-	38.5
		Area ratio	%	43.8
	Low Mol. Wt.	Mp $\times 10^{-4}$	-	5.5
		Area ratio	%	20.2
		Mp $\times 10^{-4}$	-	4.8
		Area ratio	%	36.0
	Mw/Mn		-	2.48
Conjugated diene mass ratio			%	24.0
Block rate			%	100
tan δ peak temperature			°C	-75
tan δ (max + 30 °C) / tan δ (max)			-	0.78

[0098] [Table 10]

	Sheet Blend			Sheet Impact	Dupont Impact Strength	Folding Strength	Tensile Elasticity
	Block Copolymer Resin Composition		GPPS	kJ/m	J	Times Folded	MPa
Example 1	Poly Ex 1	40 %	60 %	3.0	0.20	200	1700
Example 2	Poly Ex 2	40 %	60 %	>5.0	0.37	520	1600
Example 3	Poly Ex 3	40 %	60 %	>5.0	0.80	>1000	1100
Example 4	Poly Ex 4	40 %	60 %	2.7	0.12	140	1700
Example 5	Poly Ex 5	40 %	60 %	>5.0	0.37	>1000	1000
Example 6	Poly Ex 6	40 %	60 %	>5.0	0.37	>1000	1300
Example 7	Poly Ex 7	40 %	60 %	2.7	0.12	110	1700
Example 8	Poly Ex 8	40 %	60 %	3.6	0.28	370	1300
Example 9	Poly Ex 16	40 %	60 %	4.5	0.30	450	1700
Example 10	Blend Ex 1	40 %	60 %	>5.0	0.25	760	1550
Example 11	Poly Ex 24	40 %	60 %	4.2	0.34	410	1550
Example 12	Poly Ex 25	40 %	60 %	4.6	0.36	500	1500
Example 13	Poly Ex 2	80 %	20 %	>5.0	>0.90	>1000	1300
Example 14	Poly Ex 2	60 %	40 %	>5.0	0.71	>1000	1450
Example 15	Poly Ex 2	20 %	80 %	3.1	0.15	220	1800
Example 16	Poly Ex 2	10 %	90 %	2.7	0.10	100	1900

[0099] [Table 11]

	Sheet Blend			Sheet Impact	Dupont Impact Strength	Folding Strength	Tensile Elasticity
	Block Copolymer Resin Composition		GPPS	kJ/m	J	Times Folded	MPa
Comparative Example 1	Poly Ex 9	40 %	60 %	1.6	0.05	20	1750
Comparative Example 2	Poly Ex 10	40 %	60 %	>5.0	0.80	>1000	850
Comparative Example 3	Poly Ex 20	40 %	60 %	1.7	0.05	70	1700
Comparative Example 4	Poly Ex 11	40 %	60 %	2.3	0.05	110	1750
Comparative Example 5	Poly Ex 12	40 %	60 %	>5.0	0.30	>1000	950
Comparative Example 6	Poly Ex 13	40 %	60 %	>5.0	0.37	>1000	900
Comparative Example 7	Poly Ex 14	40 %	60 %	2.3	0.05	110	1750
Comparative Example 8	Poly Ex 22	40 %	60 %	>5.0	0.80	>1000	900
Comparative Example 9	Poly Ex 21	40 %	60 %	1.7	0.05	50	1750
Comparative Example 10	Poly Ex 15	40 %	60 %	2.5	0.09	150	1700
Comparative Example 11	Poly Ex 23	40 %	60 %	>5.0	0.36	>1000	950

INDUSTRIAL APPLICABILITY

[0100] The resin composition of the present invention and compositions blending said resin composition with various thermoplastic resins can be effectively used as materials for sheets or films, and by making use of their excellent impact resistance and mechanical properties, they can be used in a wide range of applications, such as in food packaging containers, as well as in packaging for miscellaneous goods for daily use, and as lamination sheets or films.

CLAIMS

[Claim 1] A resin composition containing a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, and satisfying the following conditions (A)-(E):
(A) the content ratio of the conjugated diene is 22 mass% to 35 mass% with respect to the entire block copolymer;
(B) the vinyl aromatic hydrocarbon block rate is 98 mass% to 100 mass%;
(C) the Mw/Mn (where Mw is the weight-average molecular weight and Mn is the number-average molecular weight) as obtained by gel permeation chromatography (GPC) using the differential refractive index method is 1.3 to 3.5;
(D) the area ratio of high-molecular-weight components in a chromatogram obtained by gel permeation chromatography (GPC) using the differential refractive index method is 30% to 55% of the total area; and
(E) the loss tangent ($\tan \delta$) as obtained by dynamic viscoelasticity measurements has one maximum value ($\tan \delta$ (max) value) within the temperature range from -100 °C to -60 °C, and the $\tan \delta$ value ($\tan \delta$ (max + 30 °C) value) at a temperature 30 °C higher than the temperature at the maximum value ($\tan \delta$ peak temperature) is 0.6 or more with respect to the $\tan \delta$ value ($\tan \delta$ (max) value) at the maximum value temperature.

[Claim 2] The resin composition according to claim 1, wherein the block copolymer comprises one or both of the vinyl aromatic hydrocarbon and conjugated diene block structures represented by the following general formulas (I) and (II):
S-(B-S)_n-B-S (I)
(S-(B-S)_n-B-S)_m-X (II)
where S denotes a polymer block having vinyl aromatic hydrocarbon monomer units; B denotes a polymer block having conjugated diene monomer units; m denotes the number of polymer chains bound to a residue of a coupling agent and is an integer greater than or equal to 1; n denotes a number of repeating units and is an integer greater than or equal to 1; and X denotes a residue of a coupling agent.

[Claim 3] The resin composition according to claim 2, wherein the block copolymer comprises all of the vinyl aromatic hydrocarbon and conjugated diene block structures represented by the following general formulas (i) to (iii):
S1-S2-S3-(B-S)_n-B-S4 (i)
S2-S3-(B-S)_n-B-S4 (ii)
S3-(B-S)_n-B-S4 (iii)

where S, S1, S2, S3 and S4 denote polymer blocks having vinyl aromatic hydrocarbon monomer units; B denotes a polymer block having conjugated diene monomer units; and n denotes a number of repeating units and is an integer greater than or equal to 1.

[Claim 4] The resin composition according to any one of claims 1 to 3 wherein the vinyl aromatic hydrocarbon is styrene and the conjugated diene is 1,3-butadiene.

[Claim 5] A resin composition containing the resin composition according to any one of claims 1 to 4 and another thermoplastic resin.

[Claim 6] The resin composition according to claim 5, wherein a content ratio (mass ratio) between the resin composition according to any one of claims 1 to 4 and the other thermoplastic resin is 10/90 to 80/20.

[Claim 7] The resin composition according to claim 5 or 6, wherein the other thermoplastic resin is a polystyrene polymer.

[Claim 8] A molded article obtained by molding the resin composition according to any one of claims 1 to 7.

[Claim 9] The molded article according to claim 8, which is a sheet, a film or an injection-molded product.

[Claim 10] A molded article obtained by secondary processing of the molded article according to claim 8 or 9.

[Claim 11] The molded article according to claim 10, which is a container, a stretched sheet or a stretched film.

[Claim 12] A molded article obtained by tertiary processing of the stretched sheet or the stretched film according to claim 11.

[Claim 13] The molded article according to claim 12, which is a container.