

BLOCK COPOLYMER COMPOSITION, HEAT-SHRINKABLE FILM, AND CONTAINER

Technical Field

[0001]

The present invention relates to a block copolymer composition, a heat-shrinkable film, and a container.

Background Art

[0002]

A heat-shrinkable film using a block copolymer consisting of a vinyl aromatic hydrocarbon monomer and a conjugated diene monomer is widely used for shrink packaging due to its excellent heat-shrinkability. Examples of the required physical property of the heat-shrinkable film include natural shrinkage resistance (resistance to dimensional changes caused by natural film shrinkage when the film is stored in an uncontrolled temperature environment), rigidity, strength (breakage resistance), and transparency. It is disclosed in Patent Literatures 1-3 that these physical properties can be satisfied in a well-balanced manner by using a block copolymer which consists of a vinyl aromatic hydrocarbon monomer and a conjugated diene monomer and has a specific polymer structure to satisfy these various required properties.

[0003]

In addition, the recent increase in the number of containers having high designability and complex design has sometimes caused attaching failures such as wrinkling, distortion, and loosening when the film is attached to the container, and a material having excellent shrinkage finishability of the film has been required. In general, the heat-shrinkable film using a block copolymer consisting of a vinyl aromatic hydrocarbon monomer and a conjugated diene monomer is considered to have better low-temperature shrinkability and shrinkage finishability than the heat-shrinkable film using a polyester-based resin, but it is difficult to achieve both natural shrinkage resistance and shrinkage finishability using a conventional technology. Therefore, improvements have been desired.

Citation List

Patent Literature

[0004]

[Patent Literature 1] JP-B-3543917
[Patent Literature 2] JP-A-2005-213520
[Patent Literature 3] JP-A-2003-313259

Summary of Invention

Technical Problem

[0005]

The present invention has been made by taking such a circumstance into consideration, and aims to provide a block copolymer composition capable of realizing a heat-shrinkable film that exhibits good heat-shrinkability and has excellent shrinkage finishability and natural shrinkage resistance. The present invention also aims to provide a heat-shrinkable film using the block copolymer composition and a container to which the heat-shrinkable film is attached.

Solution to Problem

[0006]

According to the present invention, provided is a block copolymer composition containing at least one kind of a block copolymer having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit, wherein the block copolymer composition satisfies the following (1)-(4):

(1) when the total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the block copolymer composition is taken as 100 mass%, the content of the conjugated diene monomer unit is 12-30 mass%;

(2) the weight average molecular weight in GPC measurement is 100,000-300,000 in terms of polystyrene;

(3) the loss tangent value ($\tan \delta$) in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 (General principles) and JIS K7244-5 (Flexural vibration-Non-resonance method) under the conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz has at least one peak in the range of 80-105°C; and

(4) the storage modulus (E'_{30}) at 30°C, the storage modulus (E'_{70}) at 70°C, the storage modulus (E'_{80}) at 80°C, and the storage modulus (E'_{90}) at 90°C in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under the

conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz satisfy the following relationships:

$$1400 \text{ MPa} < E'_{30} < 3000 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{70} - E'_{80}) < 400 \text{ MPa}$$

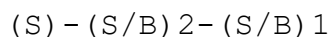
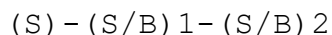
$$150 \text{ MPa} < (E'_{80} - E'_{90}) < 400 \text{ MPa}.$$

[0007]

Hereinafter, various embodiments of the present invention will be exemplified. The embodiments shown below can be combined with each other.

Preferably, E'_{70} is 400-1000 MPa, E'_{80} is 150-600 MPa, and E'_{90} is 10-300 MPa.

Preferably, the block copolymer composition contains 40-100 mass% of the block copolymer having any one of the structures represented by the following general formulas:



wherein: (S) in the general formulas represents the polymer chain of the vinyl aromatic hydrocarbon monomer unit, (S/B)₁ represents the copolymer chain containing 84-95 mass% of the vinyl aromatic hydrocarbon monomer unit and 5-16 mass% of the conjugated diene monomer unit, and (S/B)₂ represents the copolymer chain containing 40-78 mass% of the vinyl aromatic hydrocarbon monomer unit and 22-60 mass% of the conjugated diene monomer unit.

According to another aspect of the present invention, provided is a heat-shrinkable film containing the above-mentioned block copolymer composition.

According to another aspect of the present invention, provided is a container to which the above-mentioned heat-shrinkable film is attached.

Description of Embodiments

[0008]

Hereinafter, embodiments of the present invention will be explained. Various distinctive features shown in the following embodiments can be combined with each other. In addition, an invention can be established independently for each of the

distinctive features.

[0009]

1. Block Copolymer Composition

A block copolymer composition according to one embodiment of the present invention is a block copolymer composition containing at least one kind of block copolymer having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit.

[0010]

The vinyl aromatic hydrocarbon monomer unit is the constituent unit of the copolymer derived from the vinyl aromatic hydrocarbon monomer used as a raw material of the block copolymerization. Examples of the vinyl aromatic hydrocarbon monomer unit include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, α -methylstyrene, vinylnaphthalene, and vinylanthracene. In one aspect, the vinyl aromatic hydrocarbon monomer unit is preferably styrene. These monomers may be used alone, or two or more of these may be used in combination.

[0011]

The conjugated diene monomer unit is the constituent unit of the copolymer derived from the conjugated diene monomer used as a raw material of the block copolymerization. Examples of the conjugated diene monomer unit include 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene. In one aspect, the conjugated diene monomer unit is preferably 1,3-butadiene or isoprene. These monomers may be used alone, or two or more of these may be used in combination.

[0012]

The block copolymer having the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit can be obtained by a living anionic polymerization reaction using an organolithium compound as a polymerization initiator in an organic solvent. Since almost all of the vinyl aromatic hydrocarbon monomer and the conjugated diene monomer used in the polymerization reaction may be converted to a polymer in living anionic polymerization, a block copolymer having an arbitrary primary structure can be obtained by changing the amount and the order of addition thereof.

[0013]

The block copolymer composition satisfies at least the

following conditions (1) to (4). It should be noted that, in the present specification, the tilde symbol “~” is used to indicate a numerical value range that includes the numerical values listed therebefore and thereafter. Specifically, the description “X~Y” (X and Y are both numerical values) indicates that being “X or greater and Y or less”.

(1) When the total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the block copolymer composition is taken as 100 mass%, the content of the conjugated diene monomer unit is 12-30 mass%.

(2) The weight average molecular weight in GPC measurement is 100,000-300,000 in terms of polystyrene.

(3) The loss tangent value ($\tan \delta$) in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under the conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz has at least one peak in the range of 80-105°C.

(4) The storage modulus (E'_{30}) at 30°C, the storage modulus (E'_{70}) at 70°C, the storage modulus (E'_{80}) at 80°C, and the storage modulus (E'_{90}) at 90°C in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under the conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz satisfy the following relationships:

$$1400 \text{ MPa} < E'_{30} < 3000 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{70} - E'_{80}) < 400 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{80} - E'_{90}) < 400 \text{ MPa}.$$

[0014]

When the total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the block copolymer composition is taken as 100 mass%, the content of the conjugated diene monomer unit is 12-30 mass%, preferably 14-25 mass%, and more preferably 15-20 mass%. In the block copolymer composition, the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit exist as the constituent units constituting the block copolymer. When the block copolymer composition contains two or more kinds of block copolymers, the contents of the units are calculated based on the total of each monomer unit in these block copolymers. The

breakage resistance of the film to be obtained becomes good by making the content of the constituent unit derived from conjugated diene 12 mass% or more, and the natural shrinkage resistance of the film to be obtained becomes good by making the content of the constituent unit derived from conjugated diene 30 mass% or less. This is also preferable in terms of ensuring the rigidity of the heat-shrinkable film.

[0015]

The content of the conjugated diene monomer unit can be calculated from the charged amounts of the vinyl aromatic hydrocarbon monomer and the conjugated diene monomer in producing each block copolymer, and may be calculated by using a known halogen addition method. A measurement example of the general halogen addition method is as follows: the sample is dissolved in a solvent capable of completely dissolving it, then an excessive amount of iodine monochloride/carbon tetrachloride solution is added and allowed to react sufficiently, and the unreacted iodine monochloride is titrated with a sodium thiosulfate/ethanol solution. The content of the conjugated diene monomer unit is calculated from the double bond amount obtained by the above-mentioned method. For the content of the vinyl aromatic hydrocarbon unit, it is calculated by subtracting the content of the conjugated diene monomer unit from the whole sample.

[0016]

The weight average molecular weight of the block copolymer composition in GPC (gel permeation chromatography) measurement is 100,000-300,000, preferably 120,000-200,000 in terms of polystyrene. The breakage resistance and the rigidity of the heat-shrinkable film become good by making the weight average molecular weight 100,000 or more. The molding processability of the block copolymer composition becomes good by making the weight average molecular weight 300,000 or less.

[0017]

The loss tangent value ($\tan \delta$) of the block copolymer composition in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under the conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz has at least one peak in the range of 80-105°C, and preferably in the range of 90-100°C. The natural shrinkage rate of the heat-shrinkable film

to be obtained can be prevented from increasing by making the temperature at which $\tan \delta$ shows the peak 80°C or higher. The heat shrinkage rate of the heat-shrinkable film to be obtained can be sufficiently increased by making the temperature at which $\tan \delta$ shows the peak 105°C or lower.

[0018]

The storage modulus (E'_{30}) at 30°C, the storage modulus (E'_{70}) at 70°C, the storage modulus (E'_{80}) at 80°C, and the storage modulus (E'_{90}) at 90°C of the block copolymer composition in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under the conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz satisfy the following relationships. " $E'_{70}-E'_{80}$ " is the difference obtained by subtracting E'_{80} from E'_{70} . " $E'_{80}-E'_{90}$ " is the difference obtained by subtracting E'_{90} from E'_{80} .

$$1400 \text{ MPa} < E'_{30} < 3000 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{70}-E'_{80}) < 400 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{80}-E'_{90}) < 400 \text{ MPa}$$

[0019]

E'_{30} is preferably 1450-2700 MPa, more preferably 1500-2400 MPa, and even more preferably 1600-2100 MPa. $E'_{70}-E'_{80}$ is preferably 200-350 MPa. $E'_{80}-E'_{90}$ is preferably 200-350 MPa. When the storage moduli of the block copolymer composition satisfy the above-mentioned relationships, the natural shrinkage resistance of the heat-shrinkable film using the block copolymer composition becomes good. When the change in the heat shrinkage rate to the shrinkage temperature becomes gradual, appearance defects such as wrinkling and distortion after attachment do not easily occur and the shrinkage finishability becomes good. The storage moduli satisfying the above-mentioned relationships are also preferable from the viewpoint of maintaining the rigidity of the heat-shrinkable film.

[0020]

The content of the block copolymer composition according to one embodiment of the present invention is preferably 40-100 mass%, more preferably 50-100 mass%, and even more preferably 60-100 mass% of the block copolymer having any one of the primary structures

represented by the following general formulas. These primary structures have plural kinds of block chains, in which the compositions of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit continuously vary, in the same molecule. As a result, the storage modulus near the softening temperature gradually decreases and the block copolymer composition satisfying the above-mentioned storage modulus relationships is easily obtained.

(S)-(S/B)1-(S/B)2

(S)-(S/B)2-(S/B)1

[0021]

In the general formula, "(S)" is the polymer chain containing more than 95 mass% of the vinyl aromatic hydrocarbon monomer unit. Preferably, it is substantially composed of only the vinyl aromatic hydrocarbon monomer unit.

[0022]

In the general formula, "(S/B)1" is the copolymer chain containing 84-95 mass% of the vinyl aromatic hydrocarbon monomer unit and 5-16 mass% of the conjugated diene monomer unit. The composition distribution of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit may be either in a tapered state (where the microscopic composition of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit varies continuously in almost one direction) or in a random state (where the microscopic composition of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit is almost constant). In one aspect, the composition distribution is preferably in a tapered state. The composition distribution of the copolymer chain is controlled by the amount and method of addition of each monomer in polymerization. The copolymer chain in which the composition distribution is in a tapered state can be obtained by adding an excessive amount of vinyl aromatic hydrocarbon (e.g., styrene) and conjugated diene (e.g., 1,3-butadiene) to the polymerization active terminals collectively and simultaneously. The copolymer chain in which the composition distribution is in a random state can be obtained by adding the excessive amount of vinyl aromatic hydrocarbon and conjugated diene to the polymerization active terminals little by little with the flow rates constant.

[0023]

In the general formula, "(S/B)2" is the copolymer chain

containing the 40-78 mass% of the vinyl aromatic hydrocarbon monomer unit and 22-60 mass% of the conjugated diene monomer unit. The composition distribution of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit may be either in a tapered state or in a random state. In one aspect, the composition distribution is preferably in a tapered state. The composition distribution of the copolymer chain is controlled by the amount and method of addition of each monomer in polymerization.

[0024]

E'70 is preferably 400-1000 MPa, and more preferably 500-750 MPa. E'80 is preferably 150-600 MPa, and more preferably 240-450 MPa. E'90 is preferably 10-300 MPa, and more preferably 20-150 MPa. Preferably, E'70, E'80 and E'90 simultaneously satisfy the above-mentioned ranges. When E'70, E'80 and E'90 are within the above-mentioned ranges, the change in the heat shrinkage rate to the shrinkage temperature when the block copolymer composition is made into a heat-shrinkable film is likely to be more gradual, and good shrinkage finishability is likely to be exhibited.

[0025]

The block copolymers according to one embodiment of the present invention can be obtained by a living anionic polymerization reaction using an organolithium compound as a polymerization initiator in an organic solvent.

[0026]

Examples of the organic solvent include aliphatic hydrocarbons such as butane, pentane, hexane, isopentane, heptane, octane, and isooctane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane; and aromatic hydrocarbons such as benzene, toluene, ethyl benzene, and xylene.

[0027]

The organolithium compound is a compound with one or more lithium atoms bonded in a molecule. Examples of the organolithium compound include monofunctional organic lithium compounds such as ethyl lithium, n-propyl lithium, isopropyl lithium, n-butyl lithium, sec-butyl lithium, and tert-butyl lithium; and multifunctional organic lithium compounds such as hexamethylenedilithium, butadienyldilithium, and isoprenyldilithium.

[0028]

In living anionic polymerization, a block copolymer having an arbitrary primary structure can be obtained by changing the addition amount and addition method of monomers (vinyl aromatic hydrocarbon monomer and conjugated diene monomer), thereby enabling to control the physical property of the block copolymer. For example, the molecular weight can be controlled by the ratio of the organolithium compound to the monomers, and the storage modulus and loss tangent ($\tan\delta$) can be controlled by the ratio of the vinyl aromatic hydrocarbon to the conjugated diene in each block chain.

[0029]

The block copolymer thus obtained is deactivated by adding a polymerization stopper such as water, alcohol, and carbon dioxide in an amount sufficient to deactivate the active terminals. As a method of recovering the copolymer from the obtained block copolymer solution, an arbitrary method, such as (A) a method of precipitating the copolymer with a poor solvent such as methanol, (B) a method of evaporating the solvent by a heating roll or the like to precipitate the copolymer (drum dryer method), (C) a method of removing the solvent by a vent extruder after concentration of the solution by a concentrator (devolatilization and extrusion method), and (D) a method of dispersing the solution in water and recovering the copolymer by heating and removing the solvent by blowing steam (steam stripping method) can be employed. In particular, the devolatilization and extrusion method is preferable.

[0030]

The block copolymer composition according to one embodiment of the present invention is obtained by mixing at least one kind of block copolymer obtained by the above-mentioned production method or the like with other additives as needed.

[0031]

Examples of other additives include various stabilizers, lubricants, processing aids, blocking inhibitors, antistatic agents, antifogging agents, light resistance improvers, softeners, plasticizers, and pigments. Each additive may be added to the block copolymer solution, or blended with the recovered copolymer and melt-mixed.

[0032]

Examples of the stabilizer include phenolic antioxidants such as 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-

methylphenylacrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4, 6-di-tert-pentylphenylacrylate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and 2,6-di-tert-butyl-4-methylphenol; and phosphorus antioxidants such as trisnonylphenylphosphite. Examples of the blocking inhibitor, the antistatic agent, and the lubricant include fatty acid amides, ethylenebisstearamides, sorbitan monostearates, saturated fatty acid esters of aliphatic alcohols, and pentaerythritol fatty acid esters. Preferably, the used amounts of these additives are 5 mass% or less with respect to the block copolymer.

[0033]

The block copolymer composition according to one embodiment of the present invention may contain two or more block copolymers, and a known method can be employed for mixing these block copolymers. For example, they can be dry-blended with a Henschel mixer, ribbon blender, super mixer, V-blender, or the like, or further melted and pelletized by an extruder. In one aspect, melt-mixing is preferable. A method of removing the solvent after mixing polymer solutions with each other can also be used.

[0034]

2. Heat-shrinkable Film

The heat-shrinkable film according to one embodiment of the present invention is a heat-shrinkable film containing the above-mentioned block copolymer composition. The heat-shrinkable film can be obtained by uniaxial, biaxial, or multiaxial stretching of a sheet or film extruded by a known method such as a T-die method and a tubular method using the above-mentioned block copolymer composition. In particular, biaxial stretching by the T-die method is preferable.

[0035]

For the heat-shrinkable film according to one embodiment of the present invention, the layer containing the above-mentioned block copolymer composition can be used alone, and the heat-shrinkable multilayer film can be made by laminating another resin layer on at least one surface thereof. To obtain a heat-shrinkable multilayer film, the heat-shrinkable film after stretching may be laminated with another resin layer, the unstretched film obtained by forming the above-mentioned resin composition into a film may be laminated with another resin layer and stretched, or the multilayer film obtained by laminating the above-mentioned resin composition

with another resin by multilayer extrusion molding may be stretched. A styrene-based resin is preferable as a resin used for another resin layer.

[0036]

Examples of the uniaxial stretching include a method of stretching the extruded sheet in the direction perpendicular to the extrusion direction (TD) by a tenter, and a method of stretching the extruded tubular film in a circumferential direction.

[0037]

Examples of the biaxial stretching include a method of stretching the extruded sheet in the extrusion direction (MD) and then stretching it in the direction perpendicular to the extrusion direction (TD) by a tenter or the like, and a method of stretching the extruded tubular film in the extrusion direction and in the circumferential direction simultaneously or separately.

[0038]

For example, the stretching temperature is preferably 60-120°C. When the stretching temperature is 60°C or higher, the sheet or film is less likely to be broken during stretching. When the stretching temperature is 120°C or lower, the shrinkability and thickness precision of the obtained film are likely to be good. The stretching ratio is not particularly limited, and preferably 1.5-8 times. The heat-shrinkability is likely to be good when the stretching ratio is 1.5 times or higher, and the sheet or film is less likely to be broken during stretching when the stretching ratio is 8 times or lower. When such a film is used as a heat-shrinkable label or packaging material, the heat shrinkage rate is preferably 20% or higher at 80°C. The heat shrinkage rate of lower than 20% is not preferable because it needs a high temperature in shrinkage and adversely affect the article to which the film is to be attached. The thickness of the film is preferably 10-300 μm .

[0039]

The above-mentioned heat-shrinkable film can be used as a heat-shrinkable label, a heat-shrinkable cap seal, or the like. In addition, it can be used as a packaging film or the like.

[0040]

A container according to one embodiment of the present invention is a container such as a PET bottle to which the above-mentioned heat-shrinkable film is attached as a label or the like.

Example

[0041]

Hereinafter, Examples are provided to further explain the present invention. These are all exemplary and do not limit the contents of the present invention.

[0042]

[Production of Block Copolymer]

Block copolymers (P-1)-(P-8) were produced by the following operations (Table 1). When the structure (general formula) of the block copolymer is shown in Table 1, blocks are referred to as first block, second block, and third block, in order from the block on the left.

[0043]

<Block Copolymer (P-1)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 32 kg of styrene was added and anionically polymerized. The internal temperature rose to 48°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 9 kg of 1,3-butadiene and 67 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 86°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 25 kg of 1,3-butadiene and 67 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 97°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-1) having the primary structure represented by (S)-(S/B)1-(S/B)2.

(7) The polymerization liquid was devolatilized, and melted and

pelletized with an extruder to obtain the block copolymer (P-1).

[0044]

<Block Copolymer (P-2)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 32 kg of styrene was added and anionically polymerized. The internal temperature rose to 48°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 5 kg of 1,3-butadiene and 41 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 62°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 29 kg of 1,3-butadiene and 93 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 105°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-2) having the primary structure represented by (S)-(S/B)1-(S/B)2.

(7) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-2).

[0045]

<Block Copolymer (P-3)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 32 kg of styrene was added and anionically polymerized. The internal temperature rose to 48°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 25 kg of 1,3-

butadiene and 67 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 97°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 9 kg of 1,3-butadiene and 67 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 86°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-3) having the primary structure represented by (S)-(S/B)2-(S/B)1.

(7) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-3).

[0046]

<Block Copolymer (P-4)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 122 kg of styrene was added and anionically polymerized. The internal temperature rose to 95°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 32 kg of 1,3-butadiene and 46 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 87°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-4).

(6) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-4).

[0047]

<Block Copolymer (P-5)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 6 kg of styrene was added and anionically polymerized. The internal temperature rose to 32°C.

(4) After styrene was completely consumed, 30 kg of 1,3-butadiene was added collectively and anionically polymerized. The internal temperature rose to 51°C.

(5) After 1,3-butadiene was completely consumed, the internal temperature of the reaction system was raised to 80°C. Thereafter, 145 kg of styrene in total and 13 kg of 1,3-butadiene in total were added simultaneously at constant addition rates of 145 kg/h and 13 kg/h, respectively, while maintaining the internal temperature at 80°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 75°C, and then 6 kg of styrene was added collectively and anionically polymerized. The internal temperature rose to 77°C.

(7) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-5).

(8) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-5).

[0048]

<Block Copolymer (P-6)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 8 kg of styrene was added and anionically polymerized. The internal temperature rose to 34°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was raised to 80°C. Thereafter, 112 kg of styrene in total and 18 kg of 1,3-butadiene in total were added simultaneously at constant addition rates of 149 kg/h and 24 kg/h,

respectively, while maintaining the internal temperature at 80°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 45°C, and then 25 kg of 1,3-butadiene and 29 kg of styrene were added collectively and anionically polymerized. The internal temperature rose to 77°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 75°C, and then 8 kg of styrene was added collectively and anionically polymerized. The internal temperature rose to 78°C.

(7) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-6).

(8) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-6).

[0049]

<Block Copolymer (P-7)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 32 kg of styrene was added and anionically polymerized. The internal temperature rose to 48°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 5 kg of 1,3-butadiene and 41 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 63°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 10 kg of 1,3-butadiene and 44 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 65°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C. Thereafter, 19 kg of 1,3-butadiene and 49 kg of styrene were added collectively and simultaneously and anionically polymerized. The

internal temperature rose to 78°C.

(7) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-7).

(8) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-7).

[0050]

<Block Copolymer (P-8)>

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

(2) 2000 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 32 kg of styrene was added and anionically polymerized. The internal temperature rose to 48°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 13 kg of 1,3-butadiene and 63 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 93°C.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 40°C, and then 33 kg of 1,3-butadiene and 59 kg of styrene were added collectively and simultaneously and anionically polymerized. The internal temperature rose to 101°C.

(6) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 70°C, and then all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing the block copolymer (P-8).

(7) The polymerization liquid was devolatilized, and melted and pelletized with an extruder to obtain the block copolymer (P-8).

[0051]

[Table 1]

Table 1		P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
Structure of Block Copolymer		S-(S/B)1-(S/B)2		S-(S/B)2-(S/B)1		Others			
First Block	Addition Amount of Styrene	kg	32	32	32	122	6	8	32
	Addition Amount of 1,3-butadiene	kg	0	0	0	0	0	0	0
	Ratio of Styrene Monomer Unit/1,3-butadiene Monomer Unit	mass%	100/0	100/0	100/0	100/0	100/0	100/0	100/0
	Addition Method	-	Collectively Added	Collectively Added	Collectively Added	Collectively Added	Collectively Added	Collectively Added	Collectively Added
Second Block	Addition Amount of Styrene	kg	67	41	67	46	0	112	41
	Addition Amount of 1,3-butadiene	kg	9	5	25	32	30	18	5
	Ratio of Styrene Monomer Unit/1,3-butadiene Monomer Unit	mass%	88.2/11.8	89.1/10.9	72.8/27.2	59.0/41.0	0/100	86/14	89.1/10.9
	Addition Method	-	Collectively Added	Collectively Added	Collectively Added	Collectively Added	Collectively Added	Added At Constant Addition Rate	Collectively Added
Third Block	Addition Amount of Styrene	kg	67	93	67	0	145	29	44
	Addition Amount of 1,3-butadiene	kg	25	29	9	0	13	25	10
	Ratio of Styrene Monomer Unit/1,3-butadiene Monomer Unit	mass%	72.8/27.2	76.2/23.8	88.2/11.8	-	91.8/8.2	53.7/46.3	81.5/18.5
	Addition Method	-	Collectively Added	Collectively Added	Collectively Added	-	Added At Constant Addition Rate	Collectively Added	Collectively Added
Fourth Block	Addition Amount of Styrene	kg	0	0	0	0	6	8	49
	Addition Amount of 1,3-butadiene	kg	0	0	0	0	0	0	19
	Ratio of Styrene Monomer Unit/1,3-butadiene Monomer Unit	mass%	-	-	-	-	100/0	100/0	72.1/27.9
	Addition Method	-	-	-	-	-	Collectively Added	Collectively Added	Collectively Added

* In the structure (general formula) of the block copolymer shown in Table 1, blocks are referred to as first block, second block, ..., in order from the block on the left.

[0052]

[Examples 1-4 and Comparative Examples 1-5]

Each block copolymer was used to prepare the block copolymer compositions by mixing in accordance with the compositions in Table 2 by melt-kneading as needed. The content (mass%) of each block copolymer of P-1 - P-8 in Table 2 represents the ratio of each block copolymer when the total amount of the block copolymer having the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit added to the block copolymer composition is taken as 100 mass%. The styrene ratio is the ratio of the vinyl aromatic hydrocarbon monomer unit such as styrene. The butadiene ratio is the ratio of the conjugated diene monomer unit such as butadiene.

[0053]

A biaxial stretching equipment using the T-die method was used to prepare the heat-shrinkable films for various measurements and evaluations. Each of the block copolymer compositions described in Examples or Comparative Examples was extruded at a temperature of 210°C by a sheet extruder equipped with a T-die to form a sheet with a thickness of approximately 0.3 mm, and stretched by 1.2 times in the flow direction (MD) by a longitudinal stretching machine at a line speed of 10 m/min at the temperature shown in Table 2. Thereafter, it was stretched by 4.5 times in the direction perpendicular to the flow direction (TD) by a lateral stretching machine at the temperature shown in Table 2, thereby obtaining the heat-shrinkable film with an average thickness of approximately 50 μm .

[0054]

The following methods and criteria were used for physical properties and evaluations.

[0055]

[Styrene Ratio and Butadiene Ratio]

The styrene ratio and the butadiene ratio were measured and calculated by the above-mentioned halogen addition method.

[0056]

[GPC Measurement]

GPC measurements of the block copolymer compositions were performed using the following GPC measurement equipment and conditions.

Equipment Name: HLC-8220GPC (made by Tosoh Corporation)

Column: ShodexGPCKF-404 (made by Showa Denko K.K.), 4 columns connected in series

Temperature: 40°C

Detection: differential refractive index

Solvent: tetrahydrofuran

Concentration: 2 mass%

Calibration Curve: prepared using standard polystyrene (made by Varian, Inc.)

[0057]

[Dynamic Viscoelasticity Measurement]

The storage modulus (E') and the loss tangent value ($\tan \delta$) of the resin compositions were measured in accordance with the following procedure based on JIS K7244-1 and JIS K7244-5.

(1) A molded product with a thick of 4 mm and a width of 10 mm was made by injection molding using pellets of each resin composition, and a test piece with an appropriate size was cut from this molded product. It was stored in a room at 23°C at 50% RH for 48 hours for curing treatment.

(2) The storage modulus (E') and the loss modulus (E'') were measured in the temperature range from room temperature to 120°C at the temperature increase rate of 4°C/min and the measurement frequency of 1 Hz using the dynamic viscoelasticity measurement equipment RSA3 made by TA Instruments, Inc. The following formula was used to calculate $\tan \delta$ in the above-mentioned temperature range.

$$\tan \delta = E''/E'$$

[0058]

[Measurement of Heat shrinkage Rate]

The heat shrinkage rate was measured by the following method.

(1) A test piece with a MD width of 100 mm and a TD width of 100 mm was cut from the heat-shrinkable film.

(2) The test piece was completely immersed in warm water at 70°C, 80°C, 90°C, or 100°C for 10 seconds. Theater, it was removed therefrom and sufficiently wiped, and then the TD length L (mm) was measured.

(3) The heat shrinkage rate was calculated based on the following formula.

$$\text{Heat shrinkage rate (\%)} = \{(100-L)/100\} \times 100$$

[0059]

[Measurement of Natural Shrinkage Rate]

The natural shrinkage rate was measured by the following method.

(1) A test piece with a MD width of 100 mm and a TD width of 350 mm was cut from the heat-shrinkable film.

(2) Reference lines were provided at the center part of the test piece such that the TD reference line interval was 300 mm. The test piece was stored in an environmental testing machine at 40°C. The reference line interval N (mm) was measured after 7 days of storage.

(3) The natural shrinkage rate was calculated based on the following formula.

$$\text{Natural shrinkage rate (\%)} = \{(300-N)/300\} \times 100$$

[0060]

<Shrinkage Finishability>

The shrinkage finishability was determined in accordance with the following criteria. It should be noted that wrinkling is a state in which a portion of the film is not flat locally, distortion is a state in which the contour of the film differs significantly from the rectangle, and waving is a state in which the entire film is not flat almost homogeneously.

Excellent: The sample after measuring the heat shrinkage rate does not show any of wrinkling, distortion, and waving under all conditions of 70°C, 80°C, 90°C, and 100°C.

Good: The sample after measuring the heat shrinkage rate shows any of wrinkling, distortion, and waving under any one of the conditions of 70°C, 80°C, 90°C, and 100°C.

Bad: The sample after measuring the heat shrinkage rate shows any of wrinkling, distortion, and waving under two or more of the conditions of 70°C, 80°C, 90°C, and 100°C.

[0061]

<Heat-shrinkability>

The heat-shrinkability was determined in accordance with the following criteria.

Excellent: (The heat shrinkage rate at 100°C is) 70% or higher

Good: (The heat shrinkage rate at 100°C is) 60% or higher and lower than 70%

Bad: (The heat shrinkage rate at 100°C is) lower than 60%

[0062]

<Natural Shrinkage Resistance>

The natural shrinkage rate was determined in accordance with the following criteria.

Excellent: (The natural shrinkage rate at 40°C is) lower than 4%

Good: (The natural shrinkage rate at 40°C is) 4% or higher and 8% or lower

Bad: (The natural shrinkage rate at 40°C is) higher than 8%

[0063]

[Table 2]

Table 2		Example				Comparative Example				
		1	2	3	4	1	2	3	4	5
Composition	P-1	100			67					
	P-2		100							
	P-3			100						
	P-4				33	100				
	P-5						100			
	P-6							100		
	P-7								100	
	P-8									100
	Styrene Ratio	83.0	83.0	83.0	83.7	84.0	78.7	78.4	83.0	76.0
Molding Condition	Butadiene Ratio	17.0	17.0	17.0	16.7	16.0	21.5	21.5	17.0	24.0
	Weight Average Molecular Weight	17	17	17	15	14	15	15	17	15
	MD Stretching Temperature	80	80	80	80	80	80	80	80	80
	TD Stretching Temperature	90	90	90	90	95	90	90	85	90
Physical Property	tan δ Peak Temperature	97	97	96	99	110	93	72	86	91
	E'30	1530	1670	1630	1660	1700	1990	1960	1740	1180
	E'70	710	540	650	600	1110	350	23	220	230
	E'80	420	250	380	280	890	11	5	46	85
	E'90	110	50	120	30	610	2	3	8	16
	E'70-E'80	290	290	270	320	220	339	18	174	145
	E'80-E'90	310	200	260	250	280	9	2	38	69
	70°C Heat Shrinkage Rate	16	17	15	9	4	5	51	35	38
	80°C Heat Shrinkage Rate	45	40	39	30	14	41	65	58	54
	90°C Heat Shrinkage Rate	64	65	63	58	32	65	72	69	62
Evaluation	100°C Heat Shrinkage Rate	72	72	72	74	55	68	74	73	68
	40°C Natural Shrinkage Rate	6.2	8.0	6.5	3.9	3.7	2.1	11.8	17.5	26.6
	Heat-shrinkability	Excellent	Excellent	Excellent	Excellent	Bad	Good	Excellent	Excellent	Good
	Heat Shrinkage Resistance	Good	Good	Good	Excellent	Excellent	Excellent	Bad	Bad	Bad
	Shrinkage Finishability	Good	Excellent	Excellent	Good	Good	Bad	Bad	Bad	Bad

Industrial Applicability

[0064]

The heat-shrinkable film using the block copolymer composition of the present invention has good shrinkage finishability as well as an excellent balance between various physical properties such as natural shrinkage resistance and heat-shrinkage, and can be used as a label for a PET bottle or the like.

CLAIMS

1. A block copolymer composition containing at least one kind of a block copolymer having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit, wherein the block copolymer composition satisfies following (1)-(4):

(1) when a total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the block copolymer composition is taken as 100 mass%, a content of the conjugated diene monomer unit is 12-30 mass%;

(2) a weight average molecular weight in GPC measurement is 100,000-300,000 in terms of polystyrene;

(3) a loss tangent value ($\tan \delta$) in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz has at least one peak in a range of 80-105°C; and

(4) a storage modulus (E'_{30}) at 30°C, a storage modulus (E'_{70}) at 70°C, a storage modulus (E'_{80}) at 80°C, and a storage modulus (E'_{90}) at 90°C in dynamic viscoelasticity measurement measured in accordance with JIS K7244-1 and JIS K7244-5 under conditions of a temperature rising rate of 4°C/min and a frequency of 1 Hz satisfy following relationships:

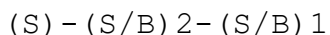
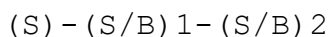
$$1400 \text{ MPa} < E'_{30} < 3000 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{70} - E'_{80}) < 400 \text{ MPa}$$

$$150 \text{ MPa} < (E'_{80} - E'_{90}) < 400 \text{ MPa}.$$

2. The block copolymer composition of Claim 1, wherein: E'_{70} is 400-1000 MPa; E'_{80} is 150-600 MPa; and E'_{90} is 10-300 MPa.

3. The block copolymer composition of Claim 1 or 2, containing 40-100 mass% of the block copolymer having any one of the structures represented by following general formulas:



wherein: (S) in the general formulas represents a polymer chain of the vinyl aromatic hydrocarbon monomer unit; (S/B)₁ represents a copolymer chain containing 84-95 mass% of the vinyl aromatic hydrocarbon monomer unit and 5-16 mass% of the conjugated diene

monomer unit; and (S/B)2 represents a copolymer chain containing 40-78 mass% of the vinyl aromatic hydrocarbon monomer unit and 22-60 mass% of the conjugated diene monomer unit.

4. The heat-shrinkable film containing the block copolymer composition of any one of Claims 1-3.

5. A container to which the heat-shrinkable film of Claim 4 is attached.