

DESCRIPTION

BLOCK COPOLYMER MIXTURE AND HEAT-SHRINKABLE FILM USING
SAME

5

TECHNICAL FIELD

The present invention relates to block copolymers each containing a vinyl aromatic hydrocarbon and a conjugated diene, a resin composition thereof, a sheet or
10 film using such a composition, and a bottle using such a film.

BACKGROUND ART

A block copolymer resin made of a vinyl aromatic
15 hydrocarbon and a conjugated diene is widely known as a resin excellent in impact strength and transparency, and it is processed into a sheet or film, followed by stretching under specific conditions to obtain a heat-shrinkable film, which is suitable for use as a packaging
20 material. However, such a block copolymer resin has a drawback that the rigidity is low, and for the purpose of overcoming the drawback, it has been common to incorporate a transparent styrene polymer (Patent Document 1). However, by the incorporation, although the
25 rigidity becomes high, there has been a drawback that the breakage resistance or shrinking properties tend to deteriorate, and the transparency has sometimes

deteriorated. (Patent Document 1: JP-A-7-268175)

DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

5 It is an object of the present invention to provide
a heat-shrinkable film and a heat-shrinkable multilayer
film, which are excellent in the balance of transparency,
breakage resistance, rigidity and heat-shrinking
properties.

10

MEANS TO ACCOMPLISH THE OBJECT

 The present inventors have conducted an extensive
study to accomplish the above object and as a result,
have found it possible to obtain a heat-shrinkable film
15 excellent in the balance of transparency, breakage
resistance, rigidity and heat-shrinking properties by
using a resin composition obtained by blending a styrene
resin with a block copolymer mixture comprising specific
amounts of three block copolymers each comprising an
20 aromatic hydrocarbon and a conjugated diene, which are
different in the molecular structures from one another.
The present invention has been accomplished on the basis
of the discovery.

 Namely, the present invention provides the
25 following:

(1) A block copolymer mixture comprising the following
block copolymers (A), (B) and (C) each containing a vinyl

aromatic hydrocarbon and a conjugated diene as constituting components, wherein (A) is from 20 to 60 mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to 50 mass%:

5 (A): a block copolymer comprising, as monomer units, from 75 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 25 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon;

10 (B): a block copolymer comprising, as monomer units, from 50 to 80 mass% of a vinyl aromatic hydrocarbon and from 20 to 50 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon; and

15 (C): a block copolymer comprising, as monomer units, from 60 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 40 mass% of a conjugated diene, and having at least one random copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic
20 hydrocarbon and from 5 to 45 mass% of a conjugated diene.

(2) A block copolymer mixture comprising the following block copolymers (A), (B) and (C) each containing a vinyl aromatic hydrocarbon and a conjugated diene as constituting components, wherein (A) is from 20 to 60
25 mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to 35 mass%:

(A): a block copolymer comprising, as monomer units,

from 75 to 90 mass% of a vinyl aromatic hydrocarbon and from 10 to 25 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average
5 molecular weight of at least 30,000 and less than 150,000;

(B): a block copolymer comprising, as monomer units, from 50 to 75 mass% of a vinyl aromatic hydrocarbon and from 25 to 50 mass% of a conjugated diene, and having, at
10 both terminals, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 1,000 and less than 30,000; and

(C): a block copolymer comprising, as monomer units, from 60 to 95 mass% of a vinyl aromatic hydrocarbon and
15 from 5 to 40 mass% of a conjugated diene, and having at least one random copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene.

20 (3) A block copolymer mixture comprising the following block copolymers (A), (B) and (C) each containing a vinyl aromatic hydrocarbon and a conjugated diene as constituting components, wherein (A) is from 20 to 60 mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to
25 50 mass%:

(A): a block copolymer with an entire number average molecular weight of at least 100,000 and less than

300,000, comprising, as monomer units, from 75 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 25 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 30,000 and less than 150,000;

(B): a block copolymer with an entire number average molecular weight of at least 50,000 and less than 200,000, comprising, as monomer units, from 50 to 80 mass% of a vinyl aromatic hydrocarbon and from 20 to 50 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 20,000 and less than 120,000, having from 10 to 70 mass% of at least one random copolymer block section comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, and further having from 15 to 45 mass% of at least one random copolymer block section comprising, as monomer units, from 0 to 55 mass% (provided that 55 mass% is excluded) of a vinyl aromatic hydrocarbon and from 45 to 100 mass% (provided that 45 mass% is excluded) of a conjugated diene; and

(C): a block copolymer with an entire number average molecular weight of at least 200,000 to less than 300,000, comprising, as monomer units, from 60 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 40 mass% of a

conjugated diene, and having at least one random copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene.

- 5 (4) The block copolymer mixture according to any one of the above (1) to (3), which has a melt flow rate of from 2 to 30 g/10 minutes.

- (5) A resin composition comprising 100 parts by mass of the block copolymer mixture as defined in the above (4)
10 and from 5 to 100 parts by mass of a styrene resin.

- (6) A sheet using the resin composition as defined in Claim 5.

- (7) A film using the resin composition as defined in the above (5).

- 15 (8) A heat-shrinkable film using the resin composition as defined in the above (5).

- (9) A heat-shrinkable multi-layer film having at least one heat-shrinkable film layer using the resin composition as defined in the above (5).

- 20 (10) A bottle having a heat-shrinkable film as defined in the above (8) put thereon.

- (11) A bottle having a heat-shrinkable multi-layer film as defined in the above (9) put thereon.

25 EFFECTS OF THE INVENTION

By using the resin composition obtained by the present invention, it is possible to obtain a film

excellent in the balance of transparency, breakage resistance, rigidity and heat-shrinking properties.

BEST MODE FOR CARRYING OUT THE INVENTION

5 (A) is a block copolymer comprising from 75 to 95 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 5 to 25 mass% of a conjugated diene, as monomer units, preferably from 80 to 90 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 10 to 20 mass% of
10 a conjugated diene, as monomer units. If the vinyl aromatic hydrocarbon exceeds 95 mass% as monomer units, or if the vinyl aromatic hydrocarbon is less than 75 mass% as monomer units, it may not be possible to obtain a sheet or film excellent in the balance of transparency,
15 breakage resistance, rigidity and heat-shrinking properties.

(A) preferably has, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of
20 at least 30,000 and less than 150,000. The number average molecular weight of such a block section is further preferably at least 50,000 and less than 100,000.

If no block section composed mainly of a vinyl aromatic hydrocarbon is present at either terminal, or
25 even if a block section composed mainly of a vinyl aromatic hydrocarbon is present, for example, at one terminal, if its number average molecular weight is less

than 30,000, the transparency of the sheet or film may sometimes deteriorate. On the other hand, if its number average molecular weight exceeds 150,000, the processability of the resin composition may sometimes
5 deteriorate.

(A) preferably has an entire number average molecular weight of at least 100,000 and less than 300,000, particularly preferably at least 120,000 and less than 240,000. If the entire number average
10 molecular weight is less than 100,000, the transparency of the sheet or film may sometimes deteriorate. On the other hand, if the entire number average molecular weight is 300,000 or higher, the processability of the resin composition may sometimes deteriorate.

15 The block proportion of (A) is not particularly limited, but is preferably from 70 to 99%. Here, the block proportion is one obtained as follows.

Block proportion = (amount of the vinyl aromatic hydrocarbon present in the form of block homopolymer
20 segments in the copolymer)/(amount of the vinyl aromatic hydrocarbon contained in the copolymer) × 100

The amount of the vinyl aromatic hydrocarbon present in the form of block homopolymer segments in the block copolymer is obtained in such a manner that in accordance
25 with an osmic acid decomposition method disclosed by L. M. Kolthoff, et. al., J. Polym. Sci., 1, 429 (1948), the block copolymer is oxidized and decomposed by tert-butyl

hydroperoxide using a catalytic amount of osmic acid, then poured into a large amount of methanol thereby to let the vinyl aromatic hydrocarbon polymer precipitate, and the precipitated polymer is vacuum-dried, whereby the
5 mass of the solid content of the vinyl aromatic hydrocarbon polymer is measured.

Further, the molecular structure of (A) is preferably linear.

(B) is preferably a block copolymer with an entire
10 number average molecular weight of at least 50,000 and less than 200,000, comprising, as monomer units, from 50 to 80 mass% of a vinyl aromatic hydrocarbon and from 20 to 50 mass% of a conjugated diene, and when it has no random copolymer block, it has, at both terminals, a
15 block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 1,000 and less than 30,000, or when it has a random copolymer block, it has, at least at one terminal, a block section composed mainly of a vinyl aromatic
20 hydrocarbon having a number average molecular weight of at least 20,000 and less than 120,000, further has at least one random copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene,
25 and further has from 15 to 45 mass% of at least one random copolymer block comprising, as monomer units, from 0 to 55 mass% (provided that 55 mass% is excluded) of a

vinyl aromatic hydrocarbon and from 45 to 100 mass% (provided that 45 mass% is excluded) of a conjugated diene.

(B) is a block copolymer comprising from 50 to 75
5 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 25 to 50 mass% of a conjugated diene, as monomer units, preferably from 55 to 75 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 25 to 45 mass% of a conjugated diene, as monomer units.

10 If the vinyl aromatic hydrocarbon as monomer units, exceeds 75 mass%, the balance of the rigidity and breakage resistance of the film tends to be poor, and if the vinyl aromatic hydrocarbon is less than 50 mass%, the decrease in the rigidity of the sheet or film may
15 sometimes be large.

When it has no random copolymer block, (B) preferably has, at both terminals, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 1,000 and
20 less than 30,000. If the number average molecular weight exceeds 30,000 or less than 1,000, the balance of the transparency, breakage resistance, rigidity and heat-shrinking properties of the sheet or film tends to be poor. On the other hand, in a case where it has a random
25 copolymer block, it preferably has, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular

weight of at least 20,000 and less than 120,000.

(B) is further preferably a block copolymer with an entire number average molecular weight of from 50,000 to less than 200,000, which has from 10 to 70 mass% of at least one random copolymer block (random block a) comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, and further has from 15 to 45 mass% of at least one random copolymer block (random block b) comprising, as monomer units, from 0 to 55 mass% (provided that 55 mass% is excluded) of a vinyl aromatic hydrocarbon and from 45 to 100 mass% (provided that 45 mass% is excluded) of a conjugated diene. If no block section composed mainly of a vinyl aromatic hydrocarbon is present at any terminal, or even if a block section composed mainly of a vinyl aromatic hydrocarbon is present at one terminal, if its number average molecular weight is less than 20,000, the transparency of the sheet or film may sometimes deteriorate. Further, if its number average molecular weight is 120,000 or higher, the processability of the resin composition may sometimes deteriorate.

Further, the entire number average molecular weight is less than 50,000, the transparency of the sheet or film may sometimes deteriorate, and if the entire number average molecular weight is 200,000 or higher, the processability of the resin composition may sometimes

deteriorate. If the vinyl aromatic hydrocarbon of the random block a exceeds 95 mass% as monomer units, the shrinking properties of the sheet or film may sometimes deteriorate, and if the vinyl aromatic hydrocarbon is
5 less than 55 mass% as monomer units, the rigidity of the sheet or film may sometimes deteriorate.

Further, if the random block a is less than 10 mass%, the shrinking properties of the sheet or film may sometimes deteriorate, and if it exceeds 70 mass%, the
10 balance of the rigidity and the breakage resistance of the sheet or film may sometimes deteriorate. If the vinyl aromatic hydrocarbon of the random block b exceeds 55 mass% as monomer units, the balance of the rigidity and the breakage resistance of the sheet or film may
15 sometimes deteriorate. Further, if this random block b is less than 15 mass%, the balance of the rigidity and the breakage resistance of the sheet or film may sometimes deteriorate, and if it exceeds 45 mass%, the decrease in the rigidity of the sheet or film may
20 sometimes be large.

Further, the molecular structure of (B) is preferably straight-chained.

(C) is a block copolymer comprising from 60 to 95 mass% of a vinyl aromatic hydrocarbon, as monomer units,
25 and from 5 to 40 mass% of a conjugated diene, as monomer units, preferably from 75 to 95 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 5 to 25 mass% of

a conjugated diene, as monomer units. If the vinyl aromatic hydrocarbon exceeds 95 mass% as monomer units, the shrinking properties of the sheet or film may sometimes deteriorate. On the other hand, if the vinyl aromatic hydrocarbon is less than 60 mass% as monomer units, the rigidity of the sheet or film may sometimes deteriorate.

The block copolymer of (C) preferably has at least one random copolymer block section comprising a vinyl aromatic hydrocarbon and a conjugated diene, and such a random copolymer block section preferably comprises from 55 to 95 mass% of a vinyl aromatic hydrocarbon, as monomer units, and from 5 to 45 mass% of a conjugated diene, as monomer units.

If the vinyl aromatic hydrocarbon of the random copolymer block section exceeds 95 mass% as monomer units, the shrinking properties of the sheet or film may sometimes deteriorate, and if the vinyl aromatic hydrocarbon is less than 55 mass% as monomer units, the rigidity of the sheet or film may sometimes deteriorate.

(C) preferably has an entire number average molecular weight of at least 200,000 and less than 300,000, more preferably at least 220,000 and less than 280,000. If the entire number average molecular weight is less than 200,000, the transparency of the sheet or film may sometimes deteriorate. On the other hand, if the entire number average molecular weight is 300,000 or

higher, the processability of the resin composition may sometimes deteriorate.

Further, the molecular structure of (C) is preferably linear.

5 In the block copolymer mixture comprising block copolymers (A), (B) and (C), (A) is from 20 to 60 mass%, preferably from 25 to 50 mass%, further preferably from 30 to 50 mass%, (B) is from 20 to 70 mass%, preferably from 25 to 60 mass%, further preferably from 30 to 55
10 mass%, and (C) is from 5 to 50 mass%, preferably from 10 to 40 mass%, further preferably from 15 to 30 mass%. If (A) is less than 20 mass%, the transparency of the sheet or film may sometimes deteriorate. If (A) exceeds 60 mass%, or if (B) is less than 20 mass%, the breakage
15 resistance of the sheet or film may sometimes deteriorate. If (B) exceeds 70 mass%, the transparency and rigidity of the sheet or film may sometimes deteriorate. If (C) is less than 5 mass%, the heat-shrinking properties of the sheet or film may sometimes
20 be inadequate, and if it exceeds 50 mass%, the breakage resistance may sometimes deteriorate.

The vinyl aromatic hydrocarbon to be used for (A), (B) and (C) may, for example, be styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-
25 dimethylstyrene, α -methylstyrene, vinyl naphthalene or vinyl anthracene, and particularly preferred is styrene. Among them, only one type may be used or two or more

types may be used in combination.

The conjugated diene to be used for (A), (B) and (C) is a diolefin having a pair of conjugated double bonds having from 4 to 8 carbon atoms, such as 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene or 1,3-hexadiene. Particularly preferred is 1,3-butadiene or isoprene. Among them, only one type may be used, or two or more types may be used in combination.

(A), (B) and (C) can be obtained by a common living anion polymerization in an organic solvent using an organic lithium compound as a polymerization initiator. The organic solvent to be used for this production is a low molecular weight organic compound composed of carbon and hydrogen, and for example, a known organic solvent may be used, such as an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane or isooctane; an alicyclic hydrocarbon such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or ethylcyclohexane; or an aromatic hydrocarbon such as benzene, toluene, ethylbenzene or xylene.

The organic lithium compound is a compound having at least one lithium atom bonded in its molecule, and it may, for example, be ethyl lithium, n-propyl lithium, isopropyl lithium, n-butyl lithium, sec-butyl lithium or tert-butyl lithium.

In the production of a block copolymer, a small

amount of a polar compound may be dissolved in the solvent. The polar compound is used to improve the efficiency of the initiator. It may, for example, be an ether such as tetrahydrofuran, diethylene glycol dimethyl
5 ether or diethylene glycol dibutyl ether; an amine such as triethylamine or tetramethylethylenediamine; a thioether; a phosphine; a phosphoramidate; an alkylbenzene sulfonate; or an alkoxide of potassium or sodium. Among them, a preferred polar compound is tetrahydrofuran.

10 The polymerization temperature for the production of the block copolymer is usually from -10 to 150°C, preferably from 40 to 120°C. The time required for the polymerization varies depending upon the conditions, but it is usually within 48 hours, preferably from 0.5 to 10
15 hours. Further, the interior of the polymerization apparatus is preferably preliminarily replaced with an inert gas such as nitrogen gas. The polymerization pressure is not particularly limited so long as the polymerization is carried out within a sufficient
20 pressure to maintain the monomer and the solvent in a liquid phase within the above mentioned polymerization temperature. Further, it is necessary to be careful for not permitting impurities which may deactivate a living polymer, such as water, oxygen, carbon dioxide gas, etc.
25 to enter into the interior of the polymerization apparatus.

After completion of the polymerization, for example,

water, an alcohol, carbon dioxide, an organic acid or an inorganic acid is added for deactivation in an amount sufficient to deactivate living active terminals.

To obtain the block copolymer mixture comprising
5 (A), (B) and (C), the polymerization liquids deactivated after completion of the polymerization of the respective block copolymers, may be mixed, followed by removal of the solvent, or the resins obtained by removing the solvents from the respective polymerization liquids, may
10 be blended with one another, followed by melt-kneading by an extruder.

To the obtained copolymer mixture, various additives may further be incorporated, as the case requires. For example, a stabilizer, a lubricant, a processing aid, a
15 blocking-preventing agent, an antistatic agent, a defogging agent, a weather resistance-improving agent, a softening agent, a plasticizer and a pigment may be mentioned. Further, these additives may be added at the time of producing a resin composition by mixing the block
20 copolymer mixture with a styrene resin.

The stabilizer may, for example, be a phenolic antioxidant such as 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-
25 methylphenyl acrylate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate or 2,6-di-tert-butyl-4-methylphenol, or a phosphorus-type antioxidant such as

2,2-methylenebis(4,6-di-tert-butylphenyl) octyl phosphite, trisnonylphenyl phosphite, or bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite.

As a lubricant, a processing aid, a blocking-
5 preventing agent, an antistatic agent or a defogging agent, for example, a saturated fatty acid such as palmitic acid, stearic acid or behenic acid; a fatty acid ester such as octyl palmitate, octyl stearate or a pentaerythritol fatty acid ester; a fatty acid amide such
10 as erucic acid amide, oleic acid amide, stearic acid amide or ethylenebis stearic acid amide; a sorbitan fatty acid ester such as a glycerol-mono-fatty acid ester, a glycerol-di-fatty acid ester, a sorbitan-mono-palmitic acid ester or a sorbitan-mono-stearic acid ester; and a
15 higher alcohol such as myristyl alcohol, cetyl alcohol or stearyl alcohol, may be used.

As a weather resistance-improving agent, an ultraviolet ray-absorber such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2,4-di-
20 tert-butylphenyl-3',5'-di-tert-butyl-4'-hydroxy benzoate or 2,-hydroxy-4-n-octoxybenzophenone, or a hindered amine type weather resistance-improving agent such as tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, may, for example, be used.

25 Further, as other additives, white oil or silicone oil may, for example, be added.

These additives are used preferably in an amount

within a range of from 0 to 5 mass% in the block copolymer mixture. If they exceed 5 mass%, the additives may bleed out on the surface of the sheet or film, whereby the appearance may be impaired.

5 The melt mass flow rate of the block copolymer mixture thus obtained is not particularly limited, but it is preferably from 2 to 30 g/10 min, more preferably from 5 to 20 g/10 min, further preferably from 5 to 15 g/10 min, from the viewpoint of the molding processability.

10 Here, the measurement was carried out in accordance with ISO 1133 under a test condition of 200°C with a load of 49 N.

 The styrene resin to be incorporated to the block copolymer mixture is a polymer having a vinyl aromatic hydrocarbon in its molecule, and it may, for example, be
15 a polystyrene, a styrene/ α -methylstyrene copolymer, an acrylonitrile/styrene copolymer, a styrene/acrylate copolymer, a styrene/methacrylate copolymer, a styrene/maleic anhydride copolymer or a styrene/butadiene
20 copolymer. Particularly preferred is a polystyrene, a styrene/acrylate copolymer or a styrene/butadiene copolymer.

 To be used for a heat-shrinkable film or a heat shrinkable multilayer film, in order to improve the
25 rigidity, it is preferred to incorporate from 5 to 100 parts by mass of the styrene resin to 100 parts by mass of the block copolymer mixture. The styrene resin is

more preferably from 10 to 80 parts by mass, further preferably from 20 to 60 parts by mass, to 100 parts by mass of the block copolymer mixture.

A known method may be employed as the method for
5 producing such a heat-shrinkable film or a heat-shrinkable multilayer film. For example, the heat-shrinkable film may be obtained by forming the resin composition into a sheet or film by a T die method or a circular die method and stretching it in a monoaxial
10 direction or biaxial directions. The heat-shrinkable multilayer film may be obtained by forming the resin composition into a sheet or film by a T die or a circular die having a feed block or a multi-manifold so that it will be at least one layer, and stretching it in a
15 monoaxial direction or biaxial directions. For a layer other than the resin composition, it is preferred to employ a styrene resin.

Further, the block copolymer mixture may be used as sheeted alone and stretched.

20 In order to obtain a good shrinking property, the stretching temperature is preferably from 60 to 120°C, and the draw ratio is preferably from 1.5 to 8 times. Further, the film thickness is preferably from 10 to 300 μm .

25 The obtained heat-shrinkable film or heat-shrinkable multilayer film may be put on a bottle as a label having a design, letters, a trademark, etc. printed by a known

method, and then, the label is heat-shrunked by a known method to fix it on the bottle. The heating method may be steam heating or hot air heating, and the heating temperature is preferably adjusted so that the label
5 surface will be from 70 to 90°C.

The heat-shrinkable film or heat-shrinkable multilayer film of the present invention may be suitably utilized as a heat-shrinkable cap seal for a bottle, a protective film for a bottle or other packaging films,
10 other than as a heat-shrinkable label for a bottle.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples. However, it
15 should be understood that the present invention is by no means restricted by such Examples. Further, it is of course possible to use a polar compound such as tetrahydrofuran also in the production of the block copolymers (B) and (C) in the following Examples in the
20 same manner as in the case of the block copolymer (A).

REFERENCE EXAMPLE 1: Production of (A)

A stainless steel polymerization tank equipped with a jacket and a stirrer and having an internal capacity of 150 L was flushed with cyclohexane and replaced by
25 nitrogen. Then, in a nitrogen gas atmosphere, 61.65 kg of cyclohexane containing 150 ppm of tetrahydrofuran and dehydrated to a water content of at most 6 ppm, was

charged into the polymerization tank, and then, 5.95 kg of styrene dehydrated to a water content of at most 5 ppm was added. The internal temperature was raised to 50°C, then 75 ml of a cyclohexane solution containing 10 mass% of n-butyl lithium was added, followed by polymerization for 20 minutes within a range where the maximum temperature did not exceed 120°C (first stage polymerization).

Further, the internal temperature was raised to 80°C, and then 9.4 kg of styrene dehydrated to a water content of at most 5 ppm and 4.1 kg of butadiene passed through a molecular sieve for dehydration were simultaneously added, followed by polymerization for 20 minutes within a range where the maximum temperature did not exceed 120°C (second stage polymerization).

Then, after termination of heat generation, under a constant condition of the internal temperature being 80°C, 1.1 kg of styrene dehydrated to a water content of at most 5 ppm was added, followed by polymerization for 20 minutes within a range where the maximum temperature did not exceed 120°C (third stage polymerization).

After termination of the polymerization, water was added to the solution to deactivate a living polymer. Then, cyclohexane was further added for dilution, and the diluted solution was poured into a large amount of methanol to precipitate the polymer content. The polymer content was separated and then dried under vacuum to

obtain a powdery block copolymer (A). This is designated as (a-1). For the number average molecular weight of the polystyrene block section, GPC (gel permeation chromatograph) of the polystyrene component obtained by
5 subjecting this polymer to ozone decomposition was measured (as the detector, an ultraviolet spectroscopic detector set at a wavelength of 254 nm, was used), and the molecular weights corresponding to the respective peaks were obtained from calibration curves prepared by
10 using standard polystyrene and styrene oligomer. When the obtained two polystyrene blocks are designated as A_1 and A_2 , their number average molecular weights were 55,000 and 10,000, respectively. Further, the entire number average molecular weight measured by GPC was
15 190,000.

By using the same method as above, block copolymers (a-2) to (a-7) as identified in Table 1 were obtained by controlling the amounts of styrene, butadiene and tetrahydrofuran. Further, the molecular weight of the
20 terminal polystyrene block was controlled by the amount of the cyclohexane solution containing 10 mass% of n-butyl lithium added. Further, in Table 1, B represents a copolymer block of styrene and butadiene, and the styrene/butadiene ratio of B is shown in the Table.

25 REFERENCE EXAMPLE 2: Production of (B) ((b-a) to (b-5))

In the same manner as in Reference Example 1, styrene and butadiene were polymerized in cyclohexane

using n-butyl lithium as an initiator and tetrahydrofuran as a random-polymerization agent, to obtain compositions as shown at (b-1) to (b-5) in Table 2-1. Further, by the same method as in Reference Example 1, block polymers (B) were separated. Their analytical values are shown in Table 2-1. The number average molecular weights of the styrene block sections were measured by the same method as in Reference Example 1.

Further, also with respect to (b-1) to (b-5), the molecular weight of the terminal polystyrene block was controlled by the amount of the cyclohexane solution containing 10 mass% of n-butyl lithium added, which was the same as used in Reference Example 1. Further, also in Table 2-1, B represents a copolymer block of styrene and butadiene, and the styrene/butadiene ratio of B is shown in the Table.

REFERENCE EXAMPLE 3: Production of (B) ((b-6) to (b-11))

The same polymerization tank as in Reference Example 1 was flushed with cyclohexane and replaced by nitrogen. Then, in a nitrogen gas atmosphere, 49 kg of cyclohexane dehydrated to a water content of at most 6 ppm and 5.67 kg of styrene dehydrated to a water content of at most 5 ppm, were charged and maintained at 30°C. Then, 152 ml of a cyclohexane solution containing 10 mass% of n-butyl lithium was added thereto, followed by polymerization. After styrene was completely consumed, the internal temperature of the reaction system was raised to 80°C,

and while the temperature was maintained, 3.99 kg in a total amount of styrene dehydrated to a water content of at most 5 ppm and 1.26 kg in a total amount of butadiene passed through a molecular sieve for dehydration were simultaneously added at constant rates of 2.6 kg/hr and 0.82 kg/hr, respectively, and after completion of the addition, the system was maintained as it was for 5 minutes. After butadiene gas was completely consumed, while the internal temperature of the reaction system was maintained at 75°C, 7.35 kg of butadiene was added all at once and continuously reacted. Further, 2.73 kg of styrene dehydrated to a water content of at most 5 ppm was added all at once and polymerized.

The solution after completion of the polymerization was treated in the same manner as in Reference Example 1 to obtain a powdery block copolymer (B). This is designated as (b-6).

Further, R_1 and R_2 shown in Table 2-2 represents the random block sections of styrene and butadiene, and the ratio of such styrene and butadiene was obtained by calculation from the monomers at the time of charging. R_1 : 76 mass% of styrene and 24 mass% of butadiene. R_2 : 0 mass% of styrene and 100 mass% of butadiene. These results are shown in Table 2-2.

Using the same method as described above, block copolymers (b-6) to (b-11) as identified in Table 2 were obtained by controlling the amounts of styrene and

butadiene.

Further, in Table 2-2, the mass% ratio of styrene to butadiene of each random block section (R_1 , R_2) is shown.

REFERENCE EXAMPLE 4: Production of (C)

5 The same polymerization tank as in Reference Example 1 was flushed with cyclohexane and replaced by nitrogen. Then, in a nitrogen gas atmosphere, 48 kg of cyclohexane dehydrated to a water content of at most 6 ppm and 0.40 kg of styrene dehydrated to a water content of at most 5
10 ppm, were charged and maintained at 30°C. Then, 155 ml of a cyclohexane solution containing 10 mass% of n-butyl lithium was added thereinto, followed by polymerization. After styrene was completely consumed, the internal temperature of the reaction system was raised to 80°C,
15 and while the temperature was maintained, 16.90 kg in a total amount of styrene dehydrated to a water content of at most 5 ppm and 2.90 kg in a total amount of butadiene passed through a molecular sieve for dehydration, were simultaneously added at constant rates of 11.1 kg/hr and
20 1.9 kg/hr, respectively, and after completion of the addition, the system was maintained as it was for five minutes. Further, 0.40 kg of styrene dehydrated to a water content of at most 5 ppm was added all at once and polymerized.

25 The solution after completion of the polymerization was treated in the same manner as in Reference Example 1 to obtain a powdery block copolymer (C). This is

designated as (c-1).

Further, the ratio of the styrene to butadiene of the random block section was obtained by calculation from the monomers at the time of charging, and they were 85
5 mass% and 15 mass%, respectively. These results are shown in Table 3.

Using the same method as described above, a block copolymer (c-2) as identified in Table 3 was obtained by controlling the amounts of styrene and butadiene.

10 EXAMPLES 1 TO 9

The block copolymers were put into a 20 L Henschel mixer and blended in the blend proportions as identified in Tables 4-1 to 4-2 so that the total amount would be 10 kg and then, extruded by a 40 mm Φ extruder (single
15 Dulmage screw, manufactured by Tabata Industrial Machinery Co., Ltd.) at a temperature of 200°C to obtain pellets of a block copolymer mixture.

Using the pellets, the melt mass flow rate was measured in accordance with ISO 1133 under a test
20 condition of 200°C with a load of 49 N.

Then, 8 kg of this block copolymer mixture and 2 kg of a commercially available GPPS (G200C, manufactured by TOYO-STYRENE CO., LTD.) were put and blended in a 20 L Henschel mixer and then extruded by a 40 mm Φ extruder
25 (single Dulmage screw, manufactured by Tabata Industrial Machinery Co., Ltd.) at a temperature of 200°C to obtain pellets of a resin composition. Using 8 kg of this resin

composition, a sheet having a thickness of 0.3 mm was formed by extrusion and transversely monoaxially stretched 4.5 times at a stretching temperature of 88°C by means of a biaxially stretching apparatus

5 (manufactured by Toyo Seiki Seisaku-Sho, Ltd.) to prepare a heat-shrinkable film (thickness: about 65 μ m), whereupon various evaluations were carried out. The results are shown in Tables 4-1 and 4-2.

Measurements of physical properties of the heat-shrinkable films in Tables 4-1 and 4-2 were carried out
10 by the following methods. Here, the tensile strain at break represents the breakage resistance of the heat-shrinkable film, and likewise, the tensile modulus represents the rigidity, the heat shrinkage represents
15 the heat shrinking property, and the haze represents the transparency.

(1) Tensile strain at break and tensile modulus:

Measured in accordance with JIS K6871 by using a TENSILON universal testing machine (RTC-1210A) manufactured by A &
20 D Co., Ltd.

(2) Heat shrinkage: A film was immersed in boiling water at 100°C for 10 seconds, whereupon the heat shrinkage was calculated by the following formula.

$$\text{Heat shrinkage (\%)} = \{(L1-L2)/L1\} \times 100$$

25 wherein L1 is the length (in stretching direction) before the immersion, and L2 is the length (in the stretching direction) after shrinkage by immersion in boiling water

at 100°C for 10 seconds.

(3) Haze: A film was cutout in a size of 50 mm × 50 mm, and the haze was measured by using a haze meter NDH2000 (manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.)

5 (in accordance with JIS K7136).

COMPARATIVE EXAMPLES 1 TO 26

In the blend proportions as shown in Tables 5-1, 5-2 and 5-3, block copolymer mixtures and resin compositions were obtained in the same manner as in Examples, and they
10 were respectively evaluated. The results are shown in Tables 5-1, 5-2 and 5-3. Here, in Table 5-1, Comparative Examples 1, 2, 4, 6, 12, 13, 15, 16, 19 and 20 are shown as Comparative Examples for convenience of preparation of the Table, but they are Working Examples of the present
15 invention.

TABLE 1

Items	Units	Reference Example 1 (block copolymer (A))						
		a-1	a-2	a-3	a-4	a-5	a-6	a-7
Amount of styrene	Mass%	80	85	80	65	95	97	80
Amount of butadiene	Mass%	20	15	20	35	5	3	20
Structure of block copolymer		A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2
Molecular weight of A1		55,000	9,000	22,000	40,000	53,000	53,000	160,000
Molecular weight of A2		10,000	87,000	8,000	10,000	9,000	9,000	10,000
Entire molecular weight		190,000	190,000	110,000	180,000	160,000	150,000	380,000
Styrene/butadiene ratio of B		70/30	71/29	73/27	52/48	92/8	95/5	64/36

TABLE 2-1

Items	Units	Reference Example 2 (block copolymer (B))				
		b-1	b-2	b-3	b-4	b-5
Amount of styrene	Mass%	65	72	65	80	40
Amount of butadiene	Mass%	35	28	35	20	60
Structure of block copolymer		A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2	A1-B-A2
Molecular weight of A1		11,000	21,000	38,000	20,000	22,000
Molecular weight of A2		5,000	8,000	9,000	9,000	10,000
Styrene/butadiene ratio of B		60/40	65/35	53/47	75/25	25/75

TABLE 2-2

Items	Units	Reference Example 2 (block copolymer (B))					
		b-6	b-7	b-8	b-9	b-10	b-11
Amount of styrene	Mass%	59	60	84	56	60	45
Amount of butadiene	Mass%	41	40	16	44	40	55
Structure of block copolymer		A1-R1-R2-A2	A1-R1-R2-A2	A1-R1-R2-A2	A1-R1-R2-A2	A1-R1-R2-A2	A1-R1-R2-A2
Molecular weight of A1		41,000	37,000	39,000	6,000	128,000	42,000
Molecular weight of A2		20,000	19,000	26,000	6,000	16,000	21,000
Entire molecular weight		152,000	148,000	144,000	150,000	320,000	150,000
Amount of R1	Mass%	25	23	52	64	40	4
Styrene/butadiene ratio of R1		76/24	70/30	75/25	75/25	75/25	75/25
Amount of R2	Mass%	35	39	3	28	35	54
Styrene/butadiene ratio of R2		0/100	15/85	0/100	0/100	0/100	0/100

TABLE 3

Items	Units	Reference Example 3 (block copolymer (C))	
		c-1	c-2
Amount of styrene	Mass%	86	50
Amount of butadiene	Mass%	14	50
Structure of block copolymer		A1-R-A2	A1-R-A2
Entire molecular weight		252,000	254,000
Amount of styrene in random copolymer block	Mass%	85	48
Amount of butadiene in random copolymer block	Mass%	15	52

TABLE 4-1

Items		Units	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Blend proportions of block copolymer mixture	a-1	Mass%	45	45		
	a-2	Mass%			45	45
	b-1	Mass%	30		30	
	b-2	Mass%		30		40
	c-1	Mass%	25	25	25	15
Melt mass flow rate of block copolymer mixture		g/10 min	5.7	5.4	5.8	6.0
Blend formulation of resin composition (block copolymer mixture/polystyrene)		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
Various properties of film using resin composition	Tensile strain at break	%	>200	>200	>200	>200
	Tensile modulus	MPa	1,590	1,680	1,700	1,610
	Heat shrinkage	%	74	73	73	72
	Haze	%	1.7	1.4	1.1	1.3

TABLE 4-2

Items		Units	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Blend formulation of block copolymer mixture	a-1	Mass%	45	35		45	
	a-2	Mass%			45		35
	b-6	Mass%	30	30	30		
	b-7	Mass%				30	30
	c-1	Mass%	25	35	25	25	35
Melt mass flow rate of block copolymer mixture		g/10 min	5.2	4.5	5.4	5.4	4.8
Blend formulation of resin composition (block copolymer mixture/polystyrene)		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
Various properties of film using resin composition	Tensile strain at break	%	>200	>200	>200	>200	>200
	Tensile modulus	MPa	1,700	>1,800	>1,800	1,760	>1,800
	Heat shrinkage	%	75	75	75	75	76
	Haze	%	2.3	2.4	1.9	2.2	2.4

TABLE 5-1

Items		Units	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Blend proportions of block copolymer mixture	a-2	Mass%	45	45	45		
	a-3	Mass%				45	
	a-4	Mass%					45
	a-5	Mass%					
	b-2	Mass%				40	40
	b-3	Mass%	40				
	b-4	Mass%		40			
	b-5	Mass%			40		
	c-1	Mass%	15	15	15	15	15
	c-2	Mass%					
Melt mass flow rate of block copolymer mixture		g/10 min	1.7	8.0	1.6	12.0	5.3
Blend formulation of resin composition (block copolymer mixture/polystyrene)		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
Various properties of film using resin composition	Tensile strain at break		>200	106	>200	>200	>200
	Tensile modulus		1,560	1,780	<1,500	<1,500	>1,500
	Heat shrinkage		67	67	73	74	74
	Haze		>5.0	1.2	>5.0	>5.0	3.7

TABLE 5-1 (Continued)

Items		Units	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10
Blend proportions of block copolymer mixture	a-2	Mass%		45	80		50
	a-3	Mass%					
	a-4	Mass%					
	a-5	Mass%	45				
	b-2	Mass%	40	40	20	85	
	b-3	Mass%					
	b-4	Mass%					
	b-5	Mass%					
	c-1	Mass%	15			15	50
	c-2	Mass%		15			
Melt mass flow rate of block copolymer mixture		g/10 min	11.1	5.2	3.6	10.2	3.6
Blend formulation of resin composition (block copolymer mixture/polystyrene)		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
Various properties of film using resin composition	Tensile strain at break	%	<100	>200	132	>200	<100
	Tensile modulus	MPa	>1,800	<1,500	1,570	<1,500	>1,800
	Heat shrinkage	%	70	71	<65	69	71
	Haze	%	1.0	2.2	1.0	>5.0	1.7

TABLE 5-2

Items		Units	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15
Blend formulation of block copolymer mixture	a-2	Mass%	35	35	35	35	
	a-3	Mass%					35
	a-4	Mass%					
	a-6	Mass%					
	a-7	Mass%					
	b-6	Mass%					30
	b-7	Mass%					
	b-8	Mass%	30				
	b-9	Mass%		30			
	b-10	Mass%			30		
	b-11	Mass%				30	
Melt mass flow rate of block copolymer mixture	c-1	Mass%	35	35	35	35	35
	c-2	Mass%					
Blend formulation of resin composition (block copolymer mixture/polystyrene) Various properties of film using resin composition		g/10 min	8.6	4.5	1.2	1.4	9.4
		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
	Tensile strain at break	%	<100	>200	>200	>200	>200
	Tensile modulus	MPa	>1,800	1,790	>1,800	<1,500	1,780
	Heat shrinkage	%	74	74	75	72	74
	Haze	%	1.0	>5.0	>5.0	>5.0	>5.0

TABLE 5-2 (Continued)

Items		Units	Comp. Ex. 16	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19
Blend formulation of block copolymer mixture	a-2	Mass%				
	a-3	Mass%	35			
	a-4	Mass%		35		
	a-6	Mass%			35	
	a-7	Mass%				35
	b-6	Mass%				30
	b-7	Mass%	30	30	30	
	b-8	Mass%				
	b-9	Mass%				
	b-10	Mass%				
	b-11	Mass%				
	c-1	Mass%	35	35	35	35
	c-2	Mass%				
Melt mass flow rate of block copolymer mixture		g/10 min	9.6	2.5	8.8	<1.0
Blend formulation of resin composition (block copolymer mixture/polystyrene)			Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
	Various properties of film using resin composition		%	>200	>200	>200
	Tensile strain at break				114	
	Tensile modulus		MPa	1,800	<1,500	>1,800
	Heat shrinkage		%	74	73	74
Haze		%	>5.0	4.4	1.2	>5.0

TABLE 5-3

Items		Units	Comp. Ex. 20	Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24	Comp. Ex. 25	Comp. Ex. 26
Blend formulation of block copolymer mixture	a-2	Mass%		35	35	80	80		
	a-3	Mass%							
	a-4	Mass%							
	a-6	Mass%							
	a-7	Mass%	35						
	b-6	Mass%		30		20		85	
	b-7	Mass%	30		30		20		85
	b-8	Mass%							
	b-9	Mass%							
	b-10	Mass%							
	b-11	Mass%							
	c-1	Mass%	35					15	15
	c-2	Mass%		35	35				
Melt mass flow rate of block copolymer mixture		g/10 min	<1.0	4.2	4.5	3.3	3.5	9.6	9.9
Blend formulation of resin composition (block copolymer mixture/polystyrene)		Mass% (parts by mass)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)	80/20 (100/25)
Various properties of film using resin composition	Tensile strain at break		%	>200	>200	168	156	>200	>200
	Tensile modulus		MPa	>1,800	<1,500	1,600	1,630	<1,500	<1,500
	Heat shrinkage		%	75	72	<65	<65	70	70
	Haze		%	>5.0	3.2	3.4	1.3	>5.0	>5.0

INDUSTRIAL APPLICABILITY

A resin composition comprising the block copolymer mixture obtained by the present invention and a styrene resin may be formed into a film, followed by stretching
5 to provide a heat-shrinkable film excellent in the breakage resistance, shrinking property and rigidity and excellent also in the balance of physical properties including transparency. Such a heat-shrinkable film or heat-shrinkable multilayer film is useful for labels for
10 plastic bottles, etc.

The entire disclosure of Japanese Patent Application No. 2005-006398 filed on January 13, 2005 including specification, claims and summary is incorporated herein
15 by reference in its entirety.

CLAIMS

1. A block copolymer mixture comprising the following
block copolymers (A), (B) and (C) each containing a vinyl
aromatic hydrocarbon and a conjugated diene as
5 constituting components, wherein (A) is from 20 to 60
mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to
50 mass%:

(A): a block copolymer comprising, as monomer units,
from 75 to 95 mass% of a vinyl aromatic hydrocarbon and
10 from 5 to 25 mass% of a conjugated diene, and having, at
least at one terminal, a block section composed mainly of
a vinyl aromatic hydrocarbon;

(B): a block copolymer comprising, as monomer units,
from 50 to 80 mass% of a vinyl aromatic hydrocarbon and
15 from 20 to 50 mass% of a conjugated diene, and having, at
least at one terminal, a block section composed mainly of
a vinyl aromatic hydrocarbon; and

(C): a block copolymer comprising, as monomer units,
from 60 to 95 mass% of a vinyl aromatic hydrocarbon and
20 from 5 to 40 mass% of a conjugated diene, and having at
least one random copolymer block comprising, as monomer
units, from 55 to 95 mass% of a vinyl aromatic
hydrocarbon and from 5 to 45 mass% of a conjugated diene.

2. A block copolymer mixture comprising the following
25 block copolymers (A), (B) and (C) each containing a vinyl
aromatic hydrocarbon and a conjugated diene as
constituting components, wherein (A) is from 20 to 60

mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to 35 mass%:

(A): a block copolymer comprising, as monomer units, from 75 to 90 mass% of a vinyl aromatic hydrocarbon and
5 from 10 to 25 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 30,000 and less than 150,000;

10 (B): a block copolymer comprising, as monomer units, from 50 to 75 mass% of a vinyl aromatic hydrocarbon and from 25 to 50 mass% of a conjugated diene, and having, at both terminals, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average
15 molecular weight of at least 1,000 and less than 30,000; and

(C): a block copolymer comprising, as monomer units, from 60 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 40 mass% of a conjugated diene, and having at
20 least one random copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene.

3. A block copolymer mixture comprising the following block copolymers (A), (B) and (C) each containing a vinyl
25 aromatic hydrocarbon and a conjugated diene as constituting components, wherein (A) is from 20 to 60 mass%, (B) is from 20 to 70 mass%, and (C) is from 5 to

50 mass%:

(A): a block copolymer with an entire number average molecular weight of at least 100,000 and less than 300,000, comprising, as monomer units, from 75 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 25 mass% of a conjugated diene, and having, at least at one terminal, a block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 30,000 and less than 150,000;

10 (B): a block copolymer with an entire number average molecular weight of at least 50,000 and less than 200,000, comprising, as monomer units, from 50 to 80 mass% of a vinyl aromatic hydrocarbon and from 20 to 50 mass% of a conjugated diene, and having, at least at one terminal, a
15 block section composed mainly of a vinyl aromatic hydrocarbon having a number average molecular weight of at least 20,000 and less than 120,000, having from 10 to 70 mass% of at least one random copolymer block section comprising, as monomer units, from 55 to 95 mass% of a
20 vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, and further having from 15 to 45 mass% of at least one random copolymer block section comprising, as monomer units, from 0 to 55 mass% (provided that 55 mass% is excluded) of a vinyl aromatic hydrocarbon and
25 from 45 to 100 mass% (provided that 45 mass% is excluded) of a conjugated diene; and

(C): a block copolymer with an entire number average

molecular weight of at least 200,000 to less than 300,000, comprising, as monomer units, from 60 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 40 mass% of a conjugated diene, and having at least one random

5 copolymer block comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene.

4. The block copolymer mixture according to any one of Claims 1 to 3, which has a melt flow rate of from 2 to 30
10 g/10 minutes.

5. A resin composition comprising 100 parts by mass of the block copolymer mixture as defined in Claim 4 and from 5 to 100 parts by mass of a styrene resin.

6. A sheet using the resin composition as defined in
15 Claim 5.

7. A film using the resin composition as defined in Claim 5.

8. A heat-shrinkable film using the resin composition as defined in Claim 5.

20 9. A heat-shrinkable multi-layer film having at least one heat-shrinkable film layer using the resin composition as defined in Claim 5.

10. A bottle having a heat-shrinkable film as defined in Claim 8 put thereon.

25 11. A bottle having a heat-shrinkable multi-layer film as defined in Claim 9 put thereon.