SPECIFICATION

BLOCK COPOLYMER COMPOSITION AND SHEET

TECHNICAL FIELD

[0001] The present invention relates to a block copolymer composition and sheet.

BACKGROUND ART

[0002] Block copolymers comprising vinyl aromatic hydrocarbons and conjugated dienes are widely used for various types of packaging such as food product containers, beverage containers, industrial containers (including various types of trays) and blister packs. Packaging often needs to be highly designable, and the content must be clearly visible, so the raw material of the packaging must have transparency and gloss. On the other hand, block copolymers comprising vinyl aromatic hydrocarbons and conjugated dienes are often mixed with vinyl aromatic hydrocarbon polymers for use in packaging, so such resin compositions also require good transparency. Concerning this problem, Patent Documents 1 and 2 describe that the use of a block copolymer comprising a vinyl aromatic hydrocarbon having a specific polymer structure and a conjugated diene is effective for solving the problem.

[0003] Furthermore, while the strength (tensile strength, impact strength) to withstand actual use is necessary for packaging applications, there are means of using block copolymers with a higher conjugated diene content for the purpose of conferring such physical properties. However, if block copolymers with a high conjugated diene content are used carelessly, the compatibility with the vinyl aromatic hydrocarbon polymers can be reduced, making it difficult to ensure good transparency and gloss.

[0004] On the other hand, as a general method of producing packaging, there is a method of melt-kneading the material, forming sheets, and thermoforming such as by vacuum forming, pressure forming or press forming to obtain various types of formed articles. These production processes include off-line systems in which sheets are

formed and wound into rolls for storage, then the sheets are unwound from the rolls and thermoformed to obtain the formed articles, and in-line systems in which the sheets are formed and immediately thermoformed without being stored in rolls to obtain the formed articles. In off-line systems, the sheets are stored for a long time in mutual contact in roll form, so when using a block copolymer comprising vinyl aromatic hydrocarbons and conjugated dienes, the sheets may stick together and become inseparable (hereinafter referred to as "blocking"). If blocking defects occur, the sheets cannot be used in subsequent thermoforming or the like, so anti-blocking properties are sought. Regarding this problem, Patent Documents 3 to 5 describe the use of a hydrocarbon wax in the block copolymer as a means for effectively preventing blocking.

[0005] However, depending on the structure of the block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene, there are cases in which sufficient anti-blocking effects cannot be obtained when arbitrarily choosing hydrocarbon waxes for use, and the use of hydrocarbon waxes suitable for the polymers used is desired.

[0006] Additionally, if the process involves storing the formed articles by stacking them on top of each other after forming the packaging, the contacting surfaces of the formed articles can stick together (hereinafter referred to as "sticking") when they are to be separated for use. This problem tends to occur when using a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene. In particular, when the recesses in the packages are deep or when the shapes of the packages are more complex, the contact area between the formed articles increases and separation becomes more difficult, so good anti-sticking properties are needed. In recent years, the use of packaging with complicated shapes has been increasing, so better anti-sticking properties have been sought in materials.

RELATED ART

Patent Documents

[0007] Patent Document 1: JP 4787480 B

Patent Document 2: JP 2006-143944 A

Patent Document 3: JP 1958261 B

Patent Document 4 : JP 2005-139326 A

Patent Document 5 : JP 4812946 B

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0008] The invention has the purpose of offering a material with a good balance of physical properties suitable for various types of packaging (including various types of trays) such as food product containers, beverage containers, industrial containers and blister packs, having excellent transparency, gloss, strength, rigidity and formability, having excellent anti-blocking properties and anti-sticking properties, and excelling in the aforementioned properties even when used in mixture with vinyl aromatic hydrocarbon-type polymers.

Means for Solving the Problems

[0009] The present invention is directed to a block copolymer composition comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein a conjugated diene content in a block copolymer component (I) having a molecular weight peak in the range of molecular weight 150,000 to 300,000 and comprising tapered blocks is 10 to 20 mass%; a conjugated diene content in a block copolymer component (II) having a molecular weight peak in the range of molecular weight 50,000 to 140,000 and comprising tapered blocks is 30 to 40 mass%; and a ratio (I)/(II) between molecular weight peak areas occupied by block copolymer component (I) and block copolymer component (II) in the block copolymer composition is 20/80 to 80/20; more preferably a block copolymer composition wherein block copolymer component (I) has a molecular weight peak in the range of molecular weight 180,000 to 290,000 and the conjugated diene content in block copolymer component (I) is 10 to 15 mass%; block copolymer component (II) has a molecular weight peak in the range of molecular weight 50,000 to 140,000 and the conjugated diene content in block copolymer component (II) is 30 to 50 mass%; and the ratio (I)/(II) between molecular weight peak areas occupied by block copolymer component (I) and block copolymer component (II) in the block copolymer composition is 40/60 to 60/40. Additionally, block copolymer component (I) comprises a vinyl aromatic hydrogen polymer block part in a molecular weight range of 80,000 to 150,000; and block copolymer component (II) comprises a vinyl aromatic hydrocarbon polymer block part in a molecular weight range of 5,000 to 40,000. Furthermore, in the present invention, the block copolymer composition comprises a total amount of 0.03 to 1.0 mass% of a single hydrocarbon wax, or at least one chosen from among hydrocarbon

waxes, stearyl stearate, stearic acid monoglyceride, erucamide and behenamide; the hydrocarbon wax is preferably a microcrystalline wax, a synthetic wax, or a mixture of a microcrystalline wax and a synthetic wax having a melting point of 60 to 120 °C, and is contained in the block copolymer composition in an amount of 0.03 to 0.5 mass%; the hydrocarbon wax has a melting point of 80 to 110 °C; and the block copolymer composition comprises a total amount of 0.03 to 0.5 mass% of a lubricant chosen from among stearyl stearate, stearic acid monoglyceride, erucamide and behenamide. Additionally, the present invention is directed to a resin composition comprising the above-described block copolymer composition and a vinyl aromatic hydrocarbon polymer at a mass ratio of 30/70 to 100/0; a sheet using this material; and a container thereof.

Effects of the Invention

[0010] By using the block copolymer composition of the present invention, it is possible to achieve excellent transparency, gloss, strength, rigidity and formability whether the block copolymer composition is used alone, or used as a mixture of the block copolymer composition and a vinyl aromatic hydrocarbon polymer. Furthermore, in addition to the above properties, it is possible to achieve better anti-blocking properties and anti-sticking properties when used as sheets and formed articles, and packaging of various shapes can be easily produced and used.

MODES FOR CARRYING OUT THE INVENTION

[0011] The block copolymer composition of the present invention has a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene as a constituent.

[0012] Examples of vinyl aromatic hydrocarbons that can be used as the block copolymer of the present invention include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, α-methylstyrene, vinylnaphthalene and vinylanthracene, among which styrene is preferred.

[0013] Examples of conjugated dienes used as the block copolymer of the present invention include 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene, among which 1,3-butadiene and isoprene are preferred.

preferably be 0.03 to 3 mass% in the block copolymer composition. At less than 0.03 mass%, sufficient anti-static properties cannot be achieved, and at more than 3 mass%, there is excessive bleed-out of the anti-static agent, which leads to a poor appearance and is therefore undesirable.

[0051] The block copolymer composition obtained in this way may be used in mixture with a vinyl aromatic hydrocarbon polymer as needed, the block copolymer composition/vinyl aromatic hydrocarbon polymer being mixable at a mass ratio of 30/70 to 100/0. If the mass ratio of the block copolymer composition is lower than 30, the strength becomes too low for practical use.

[0052] Examples of vinyl aromatic hydrocarbon polymers that can be mixed with the block copolymer composition of the present invention include vinyl aromatic hydrocarbon polymers, copolymers of vinyl aromatic hydrocarbons and acrylic acid esters, and copolymers of vinyl aromatic hydrocarbons and methyl methacrylate, among which representative examples are polystyrenes, styrene/n-butylacrylate copolymers, and styrene/methyl methacrylate copolymers. Among these, polystyrenes are most commonly used.

[0053] The block copolymer composition of the present invention may be used favorably in various types of formed articles, whether alone or as a mixture with vinyl aromatic hydrocarbon polymers. Examples of the method of production of the formed articles include a T-die process, inflation with an annular die, casting or calendering to produce a sheet, then subjecting the sheet to a publicly known thermoforming process such as vacuum forming, pressure forming, press forming or hot-plate forming to obtain various types of formed articles, or subjecting to publicly known injection molding processes to obtain various types of formed articles. They can also be used in applications for storing formed articles by stacking.

[0054] The sheet using a resin composition comprising a block copolymer composition and a vinyl aromatic hydrocarbon polymer according to the present invention is not particularly restricted as to its thickness, but will normally be used in the range of 0.05 mm to 5 mm. If the thickness is less than 0.05 mm, the rigidity and strength of the sheet will be too low, and if more than 5 mm, the sheet can be difficult to thermoform into formed articles and is thus impractical. More preferably, the thickness is 0.1 mm to 1.5 mm.

[0055] In the resin composition comprising a block copolymer composition and a vinyl aromatic hydrocarbon polymer according to the present invention, the amount of vinyl aromatic hydrocarbon polymer added is chosen in consideration of the balance of strength, rigidity and cost needed in the packaging. Examples of important physical properties not dependent on the amount of vinyl aromatic hydrocarbon polymer added are haze and gloss.

[0056] As an example of a preferable range of haze in the sheets used in the resin composition of the present invention, the haze in a sheet of thickness 0.6 mm should preferably be 7% or less, and more preferably 5% or less. If the haze exceeds 7%, there is an extreme decrease in the macroscopic transparency, reducing the designability, which is undesirable.

[0057] Furthermore, as an example of a preferable range of gloss in the sheets used in the resin composition of the present invention, the gloss in a sheet of thickness 0.6 mm should preferably be at least 150, and more preferably at least 160. If the gloss is less than 150, there is an extreme reduction in the macroscopic glossiness, reducing the designability, which is undesirable.

[0058] An indicator of the strength of the sheet is the tensile elongation when using a tension testing machine. As an example of a preferable range of tensile elongation in a sheet using the resin composition of the present invention, the tensile elongation in the manufacturing direction of the sheet measured at a tension speed of 10 mm/min in a 0.6 mm thick sheet should preferably be at least 20%. If less than 20%, the strength of the sheet can be deficient, making it difficult to use in practice. The aforementioned tensile elongation is more preferably in the range of at least 50%.

[0059] An indicator of the rigidity of the sheet is the modulus of tensile elasticity obtained in the same manner as the measurement of the tensile elongation. As an example of a preferable range for the modulus of tensile elasticity in a sheet using the resin composition of the present invention, the modulus of tensile elasticity in the manufacturing direction of the sheet measured at a tension speed of 10 mm/min in a 0.6 mm thick sheet should preferably be 500 to 2500 MPa, more preferably 1000 to 2000 MPa. If less than 500 MPa, the rigidity of the sheet and the glass transition temperature become too low, leading to reduced formability. If more than 2500 MPa, the strength of the sheet can be too low, making it difficult to use in practice.

complete the polymerization.

[0065] Reference Example 4 (Block Copolymer (D)) and Reference Example 11 (Block Copolymer (K)) were produced with reference to the production method of Reference Example 2. The amounts of the raw materials loaded are shown in Table 1.

[0066] [Reference Example 3] Production of Block Copolymer (C)

(1) 518 kg of cyclohexane were loaded into a reaction container.

(2) While stirring at an internal temperature of 30 °C, 1360 mL of n-butyllithium (10 mass% cyclohexane solution) were added, 9.1 kg of styrene monomer were added, and the temperature was raised to polymerize.

(3) At an internal temperature of 65 °C, 3.6 kg of butadiene monomer were added, then the temperature was raised to polymerize.

(4) At an internal temperature of 40 °C, 27.3 kg of butadiene monomer and 23.3 kg of styrene monomer were simultaneously added, and the internal temperature was raised within a range not greatly exceeding 80 °C to polymerize.

(5) At an internal temperature of 40 °C, 118.7 kg of styrene monomer were added to complete the polymerization.

[0067] Reference Example 7 (Block Copolymer (G)) and Reference Example 8 (Block Copolymer (H)) were produced with reference to the production method of Reference Example 3. The amounts of the raw materials loaded are shown in Table 1.

[0068] [Reference Example 5] Production of Block Copolymer (E)

(1) 367.5 kg of cyclohexane were loaded into a reaction container.

(2) While stirring at an internal temperature of 30 °C, 780 mL of n-butyllithium (10 mass% cyclohexane solution) were added, 5.5 kg of styrene monomer were added, and the temperature was raised to polymerize.

(3) At an internal temperature of 40 °C, 16.9 kg of butadiene monomer and 22.8 kg of styrene monomer were simultaneously added, and the internal temperature was raised within a range not greatly exceeding 70 °C to polymerize.

(4) At an internal temperature of 40 °C, 112.3 kg of styrene monomer were added to complete the polymerization.

[0069] [Reference Example 6] Production of Block Copolymer (F)

(1) 367.5 kg of cyclohexane were loaded into a reaction container.

(2) While stirring at an internal temperature of 30 °C, 780 mL of n-butyllithium (10

[0074] The structural characteristics of the block copolymers A to O obtained in this way are shown in Table 1. Regarding the structure of the block copolymer in Table 1, A1 and A2 respectively represent polystyrene blocks, B represents a polybutadiene block, C represents a tapered block comprising styrene and butadiene, Cr represents a random block comprising styrene and butadiene, and X represents a coupling center. The molecular weights of the respective block copolymers, the proportion of conjugated diene in the block copolymer, and the molecular weight of the polymer block portion of the vinyl aromatic hydrocarbon were measured in accordance with the methods described below.

CLAIMS

[1] A block copolymer composition comprising a vinyl aromatic hydrocarbon and a conjugated diene, wherein a conjugated diene content in a block copolymer component (I) having a molecular weight peak in the range of molecular weight 150,000 to 300,000 and comprising tapered blocks is 10 to 20 mass%; a conjugated diene content in a block copolymer component (II) having a molecular weight peak in the range of molecular weight 60,000 to 100,000 and comprising tapered blocks is 30 to 50 mass%; and a ratio (I)/(II) between molecular weight peak areas occupied by block copolymer component (I) and block copolymer component (II) in the block copolymer composition is 20/80 to 80/20.

[2] The block copolymer composition of claim 1, wherein block copolymer component (I) has a molecular weight peak in the range of molecular weight 180,000 to 290,000 and the conjugated diene content in block copolymer component (I) is 10 to 15 mass%; block copolymer component (II) has a molecular weight peak in the range of molecular weight 60,000to 100,000 and the conjugated diene content in block copolymer component (II) is 30 to 40 mass%; and the ratio (I)/(II) between molecular weight peak areas occupied by block copolymer component (I) and block copolymer component (II) in the block copolymer composition is 40/60 to 60/40.

[3] The block copolymer composition of claim 1 or claim 2, wherein block copolymer component (I) comprises a vinyl aromatic hydrogen polymer block part in a molecular weight range of 80,000 to 150,000; and block copolymer component (II) comprises a vinyl aromatic hydrocarbon polymer block part in a molecular weight range of 5,000 to 40,000.

[4] The block copolymer composition of any one of claims 1 to 3, comprising a total amount of 0.03 to 1.0 mass% in the block copolymer composition of a single hydrocarbon wax, or at least one chosen from among hydrocarbon waxes, stearyl stearate, stearic acid monoglyceride, erucamide and behenamide.