

FOAMED FILM, HEAT SHRINKABLE FILM, AND LABEL

Technical Field

[0001]

The present invention relates to a foamed film, a heat shrinkable film, and a label.

Background Art

[0002]

A label is used for PET bottled beverages and the like, and there is a need to enhance separability between a bottle and a label to enhance recyclability of a PET bottle. In Patent Literature 1, disclosed is a label with a foamed film as a separable label in water.

Citation List

Patent Literature

[0003]

[Patent Literature 1] JP-B-4813181

Summary of Invention

Technical Problem

[0004]

However, surface smoothness has been a problem in a foamed film when performing printing on the surface.

[0005]

The present invention has been made by taking such a circumstance into consideration, and provides a foamed film with excellent surface smoothness and low specific gravity. The present invention also provides a heat shrinkable film and a label using the said foamed film, as well as having excellent surface smoothness even after further stretched.

Solution to Problem

[0006]

According to the present invention, provided is (1) a foamed film, comprising: a foamed layer; and a non-foamed layer, wherein: a first resin composition constituting the foamed layer contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon

monomer unit and a conjugated diene monomer unit; a melt mass flow rate of the first resin composition at 200°C under a load of 5 kg is 5.0-15.0 g/10 min; a second resin composition constituting the non-foamed layer contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit; a melt mass flow rate of the second resin composition at 200°C under a load of 5 kg is 2.0-7.0 g/10 min; and specific gravity of the foamed film is 0.8 or higher and lower than 1.0. 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".

[0007]

The following are examples of various embodiments of the present invention. The embodiments shown below can be combined with each other.

Preferably,

(2) The foamed film of (1), wherein the melt mass flow rate of the first resin composition at 200°C under a load of 5 kg is higher than that of the second resin composition at 200°C under a load of 5 kg.

(3) The foamed film of (1) or (2), wherein the first resin composition and/or the second resin composition contain(s) 10-40 mass% of the conjugated diene monomer unit when a total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in each composition is taken as 100 mass%.

(4) A heat shrinkable film using the foamed film of any one of (1)-(3).

(5) A label using the foamed film of any one of (1)-(3) or the heat shrinkable film of (4).

Brief Description of Drawings

[0008]

Figs. 1A-1C are schematic diagrams on an example of a lamination structure of a foamed film. Fig. 1A is an example of the foamed film with non-foamed layers provided on both surfaces of the foamed layer. Fig. 1B is an example of the foamed film with the non-foamed layer provided on one surface of the foamed layer. Fig. 1C is an example of the foamed film with the non-foamed layer provided

on the foamed layer via another layer.

Description of Embodiments

[0009]

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.

[0010]

1. Foamed Film

A foamed film according to one embodiment of the present invention has a foamed layer and a non-foamed layer. The foamed film may have a plurality of foamed layers and a plurality of non-foamed layers. The foamed film may also be provided with a layer other than the foamed layer and the non-foamed layer. Preferably, at least one of the non-foamed layers is used as a front layer.

[0011]

Figs. 1A-1C are schematic diagrams on an example of a lamination structure of the foamed film. Fig. 1A is an example of the foamed film with non-foamed layers provided on both surfaces of the foamed layer. Fig. 1B is an example of the foamed film with the non-foamed layer provided on one surface of the foamed layer. Fig. 1C is an example of the foamed film with the non-foamed layer provided on the foamed layer via another layer. The non-foamed layer may be provided on the foamed layer directly or via another layer.

[0012]

Here, another layer may be an intermediate layer constituted by one or more layers. Another layer may be an undercoat layer, such as an adhesive layer capable of bonding layers to each other.

[0013]

The overall thickness of the foamed film is preferably 30-200 μm , and more preferably 50-150 μm .

[0014]

The thickness of the foamed layer in the foamed film is preferably 20-190 μm , and more preferably 30-140 μm . The thickness of 20 μm or larger is preferable because the film having low specific gravity is easily obtained, and the thickness of 190 μm or smaller is preferable because wrinkles are less likely to be generated during

processing, attaching the film to a container as a label, or the like and the film with excellent appearance is obtained.

[0015]

The layer ratio (the ratio of thicknesses of each layer) of the multilayer film is not particularly limited. The thickness of the non-foamed layer is preferably 75% or less of the overall thickness for obtaining the foamed film with low specific gravity, and is preferably 5% or more for obtaining excellent surface smoothness.

[0016]

For example, the foamed film in Fig. 1A is a foamed film with a three-layer structure in which a non-foamed layer 3 and a non-foamed layer 4 are provided on each surface of a foamed film 1. In such a film, the ratio of the thicknesses $[d_1/d_2/d_3]$ is, for example, $[1/38/1]$ - $[1/1/1]$, and preferably $[1/5/1]$ - $[1/1/1]$, where d_1 , d_2 , and d_3 represent the thicknesses of the non-foamed film 3, the foamed film 1, and the non-foamed film 4, respectively.

[0017]

The specific gravity of the foamed film is 0.8 or higher and lower than 1.0, and preferably 0.82-0.95. The foamed film having excellent surface smoothness and low specific gravity can be provided by making the specific gravity within such a range. The specific gravity of 0.8 or higher is preferable because the film having excellent surface smoothness is obtained, and the specific gravity lower than 1.0 is preferable because the film therewith can be separated from the film having the specific gravity of 1.0 or higher by water based on specific gravities.

[0018]

The foamed film is the layer constituted by the first resin composition. The first resin composition contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit.

[0019]

The melt mass flow rate of the first resin composition at 200°C under a load of 5 kg (first MFR) is 5.0-15.0 g/10 min, preferably 8.0-14.0 g/10 min, and more preferably 10.0-14.0 g/10 min. The foamed film having surface smoothness suitable for printing can be obtained by making the first MFR within such a range. The first MFR is, specifically for example, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0,

13.0, 14.0, or 15.0 g/10 min, and may be in the range between the two values exemplified herein.

[0020]

When the total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the first resin composition is taken as 100 mass%, the content of the conjugated diene monomer unit in the first resin composition is preferably 10-40 mass%, and more preferably 15-30 mass%.

[0021]

The non-foamed layer is the layer constituted by the second resin composition. The second resin composition contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit.

[0022]

The melt mass flow rate of the second resin composition at 200°C under a load of 5 kg (second MFR) is 2.0-7.0 g/10 min, and preferably 4.0-6.0 g/10 min. The foamed film having an excellent film-forming property and surface smoothness suitable for printing can be obtained by making the second MFR within such a range. The second MFR is, specifically for example, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, or 7.0 g/10 min, and may be in the range between the two values exemplified herein.

[0023]

When the total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in the second resin composition is taken as 100 mass%, the content of the conjugated diene monomer unit in the second resin composition is preferably 10-40 mass%, and more preferably 15-30 mass%.

[0024]

The block copolymer contained in the first resin composition or the second resin composition is the block copolymer having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit. The block copolymer is the copolymer synthesized by block copolymerization of a vinyl aromatic hydrocarbon monomer and a conjugated diene monomer. The block copolymer is the copolymer having one or more kinds of block chains constituted by the vinyl aromatic hydrocarbon monomer unit and/or the conjugated diene monomer unit.

[0025]

The vinyl aromatic hydrocarbon monomer unit is the constituent

unit of the copolymer derived from the vinyl aromatic hydrocarbon monomer used in 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.

[0026]

The conjugated diene monomer unit is the constituent unit of the copolymer derived from the conjugated diene monomer used in 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.

[0027]

The overall structure of the block copolymer and the structure of the polymer block constituting the block copolymer are not particularly limited. The structure of the polymer block may be the polymer block consisting mainly of the vinyl aromatic hydrocarbon monomer unit (e.g., styrene unit), the polymer block consisting mainly of the conjugated diene monomer unit (e.g., 1,3-butadiene unit), the polymer block with a random structure in which the vinyl aromatic hydrocarbon monomer unit (e.g., styrene unit) and the conjugated diene monomer unit (e.g., 1,3-butadiene unit) are randomly arranged, or the polymer block with a tapered structure in which the vinyl aromatic hydrocarbon monomer unit (e.g., styrene unit) and the conjugated diene monomer unit (e.g., 1,3-butadiene unit) are arranged in a tapered state with the distribution density graded. The overall structure of the block copolymer has a structure having at least two or more kinds of polymer blocks. The kind of the polymer block and the order in which the polymer blocks are linked are not particularly limited. The polymer blocks may be linked in a linear shape, or in a branched shape or in a star shape. For example, the polymer block with a random structure having the styrene unit and the 1,3-butadiene unit can be obtained by continuously adding small amounts of styrene and 1,3-butadiene simultaneously to the

polymerization active terminals and by polymerizing them. In addition, for example, the polymer block with a tapered structure having the styrene unit and the 1,3-butadiene unit can be obtained by collectively adding excessive amounts of styrene and 1,3-butadiene simultaneously to the polymerization active terminal and by polymerizing them. Furthermore, the overall structure of the block copolymer can be made branched or star-shaped by using a multifunctional initiator or a coupling agent.

[0028]

The number average molecular weight of the block copolymer is preferably 40,000-500,000, more preferably 80,000-300,000. The number average molecular weight of 40,000 or more is preferable because it allows to obtain sufficient rigidity and impact resistance of a block copolymer composition. The number average molecular weight of 500,000 or less is preferable because it allows to obtain a block copolymer composition having excellent processability. It should be noted that the number average molecular weight of the block copolymer can be measured using gel permeation chromatography (hereinafter abbreviated as GPC).

[0029]

The melt mass flow rate of the first resin composition at 200°C under a load of 5 kg is higher than that of the second resin composition at 200°C under a load of 5 kg. In other words, satisfaction of the relationship "first MFR > second MFR" is preferable.

[0030]

The production method of the block copolymer according to one embodiment of the present invention is not particularly limited. It is, for example, a method in which the above-mentioned vinyl aromatic hydrocarbon monomer and the conjugated diene monomer are polymerized in an organic solvent using an organolithium compound as an initiator.

[0031]

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, ethylbenzene, and xylene.

[0032]

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.

[0033]

In so-called living anionic polymerization using an organolithium compound as an initiator, almost all of the vinyl aromatic hydrocarbon and the conjugated diene used in the polymerization reaction may be converted to a polymer.

[0034]

The molecular weight of the polymer is controlled by the added amount of the organolithium compound, and a polymer that meets the desired melt mass flow rate can be obtained by adjusting the added amount. A mixture that meets the desired melt mass flow rate may be obtained by melt-mixing a plurality of resins.

[0035]

Furthermore, a randomizing agent may be added to control the polymerization state. Tetrahydrofuran (THF) is mainly used as the randomizing agent, but other ethers, amines, thioethers, phosphoramides, alkylbenzenesulfonates, alkoxides of potassium or sodium, and the like can also be used. Examples of the suitable ethers include dimethyl ether, diethyl ether, diphenyl ether, diethylene glycol dimethyl ether, and diethylene glycol dibutyl ether, in addition to THF. Tertiary amines such as trimethylamine, triethylamine, and tetramethylethylenediamine, as well as cyclic amines can be used as the amines. Triphenylphosphine, hexamethylphosphoramide, potassium alkylbenzenesulfonate or sodium alkylbenzenesulfonate, potassium butoxide or sodium butoxide, and the like can also be used as the randomizing agent.

[0036]

For example, 0.001-10 parts by mass of the randomizing agent can be added with respect to 100 parts by mass of all charged monomers. The timing of addition may be before the start of the polymerization reaction or before the polymerization of the copolymer chain. Further addition can also be performed as needed.

[0037]

The block copolymer thus obtained is deactivated by adding a polymerization terminator 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, 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.

[0038]

The first resin composition or the second resin composition 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.

[0039]

Examples of other additives include various stabilizers, lubricants, processing aids, blocking inhibitors (anti-blocking agents), 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.

[0040]

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.

[0041]

The first resin composition or the second resin composition

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.

[0042]

The production method of the foamed film is not particularly limited. For example, the method of forming the foamed film by co-extruding the foamed layer and the non-foamed layer using the first resin composition and the second resin composition can be used. In this method, they may be co-extruded with the resin composition constituting another layer. The foamed film may be produced by extruding each layer one by one or several layers at once and then laminating them.

[0043]

The method of forming the foamed layer is not particularly limited. Generally used methods, i.e., a chemical foaming method in which the resin is foamed by gas generated by thermal decomposition of the chemical foaming agent when the resin and the chemical foaming agent are melted-kneaded, and a physical foaming method in which gas is injected into the melted resin in the extruder to cause foaming, and the like can be used.

[0044]

Specific examples of the chemical foaming agent used in the chemical foaming method include baking soda, organic acids such as citric acid, azodicarbonamide, azobisisobutyronitrile, diazoaminobenzene, N,N'-dinitrosopentamethylenetetraamine, N,N'-dimethyl-N,N'-dinitroterephthalamide, benzenesulfonylhydrazide, p,p'-oxibisbenzenesulfonylhydrazide, and carbonates. Two or more of these may be mixed and used. Baking soda or a mixture of baking soda and sodium citrate is preferably used, and the foaming gas generated is carbonic acid gas. The method of adding the chemical foaming agent is not particularly limited, and may be any of the following methods: the dry-blending method into the resin pellet, the addition method using a constant feeder in the extruder hopper, or the method of making a master batch (foaming agent master batch) based on the same resin as the main raw material and adding it. The added amount of

the chemical foaming agent is appropriately adjusted based on the desired foaming ratio and the amount of gas generated by the foaming agent.

[0045]

Specific examples of the physical foaming agent used in the physical foaming method include carbonic acid gas, propane, butane, n-pentane, dichlorodifluoromethane, dichloromonofluoromethane, trichloromonofluoromethane, methanol, ethanol, and water, and carbonic acid gas is preferably used in terms of safety. Examples of the method of adding the physical foaming agent include the supplying method to the center zone of the extruder or to the center zone of the first stage extruder if a tandem extruder is used. The method of feeding the foaming gas-impregnated resin pellet to the extruder to obtain the foamed film may also be used. The added amount of the physical foaming agent is appropriately adjusted based on the desired foaming ratio.

[0046]

2. Heat Shrinkable Film

The heat shrinkable film according to one embodiment of the present invention is a film using the above-mentioned film. The heat shrinkable film is the above-mentioned foamed film (heat shrinkable foamed film) that has been stretched. The specific gravity of the foamed film hardly changes when stretched. However, the stress distribution during stretching is not necessarily uniform due to the presence of foam in the foamed layer, and therefore the smoothness of the original foamed film tends to be deteriorated. The heat shrinkable film according to one embodiment of the present invention is a heat shrinkable film that maintains the surface smoothness suitable for printing even after stretched.

[0047]

In one aspect, the heat shrinkable film may be produced by stretching each layer and then laminating them. A general lamination method such as a method using an adhesive and a method using heat can be used. However, an excessively high temperature is not preferable because it causes the heat shrinkable film to shrink. The lamination temperature is not particularly limited. Preferably, the lamination temperature is lower than 70°C. In another aspect, the heat shrinkable film may be produced by stretching the foamed film which is the multilayer film after co-extrusion or lamination. In

the present specification, the terms "sheet" and "film" are not distinguished in terms of the difference in thickness, but when the thickness changes (becomes thinner) due to the operation such as stretching, the object before becoming thinner may be referred to as "sheet".

[0048]

Stretching may be performed uniaxially, biaxially, or multiaxially. Examples of the uniaxial stretching include a method of stretching the extruded foamed sheet in the direction perpendicular to the extrusion direction (TD direction) by a tenter, a method of stretching the extruded tubular foamed film in a circumferential direction, and a method of stretching the extruded foamed sheet in the extrusion direction (MD direction) by a roll. Examples of the biaxial stretching include a method of stretching the extruded foamed sheet in the extrusion direction (MD direction) and then stretching it in the direction perpendicular to the extrusion direction (TD direction) by a tenter or the like, and a method of stretching the extruded tubular foamed film in the extrusion direction and in the circumferential direction, simultaneously or separately.

[0049]

For example, the stretching temperature is preferably 60-120°C. The stretching temperature of 60°C or higher is preferable because the film is less likely to be broken during stretching, and the stretching temperature of 120°C or lower is preferable because the film having excellent shrinkability is obtained. Particularly preferred is the range of $T_g+5^{\circ}\text{C}$ - $T_g+20^{\circ}\text{C}$ to the glass transition temperature (T_g) of the composition constituting the film. For the multilayer film, preferred is the range of $T_g+5^{\circ}\text{C}$ - $T_g+20^{\circ}\text{C}$ to T_g of the polymer composition of the layer having the lowest T_g . The glass transition temperature (T_g) can be determined, for example, from the peak temperature of the loss modulus.

[0050]

The stretching ratio is not particularly limited, and preferably 1.5-8 times. The stretching ratio of 1.5 times or higher is preferable because it allows to obtain the film having excellent shrinkability, and the stretching ratio of 8 times or lower is preferable because it allows to produce the stretched film easily. In one aspect, the heat shrinkage rate of the heat shrinkable film

is preferably 65% or higher at 100°C in 10 seconds. When the heat shrinkable film is used as a heat shrinkable label or a packaging material, the heat shrinkage rate is preferably 10% or higher at 70°C in 10 seconds. With the thermal shrinkage rate of 10% or higher, high temperature is not required during shrinkage, thus suppressing the influence on the article to be coated. The preferred thermal shrinkage rate is 15% or higher at the same temperature. Furthermore, in one aspect, the thermal shrinkage rate is preferably 65% or higher at 100°C in 10 seconds. In addition, in one aspect, the natural shrinkage rate is preferably 2.5% or lower at 40°C in 7 days.

[0051]

The overall thickness of the heat shrinkable film is preferably 30-200 μm , and more preferably 50-150 μm .

[0052]

3. Others

The foamed film and the heat shrinkable film can be used as a label, a cap seal, another packaging material, or the like.

[0053]

The heat shrinkable label using the heat shrinkable film as a label can be made by a known method, for example, by printing the stretched film and solvent-sealing it with the stretched direction taken as the circumferential direction. It can also be made by laminating the pre-printed heat shrinkable label on the non-stretched foamed film and then solvent-sealing it with the direction of large shrinkage taken as the circumferential direction.

[0054]

The label is not particularly limited, and can be used for metal can containers such as containers made of tinplate, TFS, aluminum, and the like (3-piece cans and 2-piece cans, or bottle cans with lids, etc.), glass containers, or resin-made containers such as containers made of polyethylene terephthalate (abbreviated as PET), polyethylene, and the like.

[0055]

The foamed film and the heat shrinkable film (especially the heat shrinkable film) have the advantage of excellent recyclability because their specific gravities are lower than 1 and therefore they can be separated from the container in water when used as a PET bottle label.

Examples

[0056]

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

[0057]

[Preparation of Block Copolymer: P-1]

(1) 250.0 kg of cyclohexane and 35.0 g of tetrahydrofuran (THF) were charged into a reaction vessel.

(2) 960 mL of 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 17 kg of styrene was added and anionically polymerized. The internal temperature rose to 72°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 30°C, and 60 kg of styrene and 23 kg of 1,3-butadiene were added collectively and simultaneously. The internal temperature rose to 100°C.

(5) After styrene and 1,3-butadiene were completely consumed, all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing a block copolymer having a polystyrene block and a tapered block of styrene and butadiene.

(6) The polymerization liquid was preconcentrated and further devolatilized and extruded by a twin-screw extruder with a vacuum vent to obtain the desired pelletized block copolymer (P-1).

[0058]

<Number Average Molecular Weight>

The number average molecular weight was measured by GPC under the following conditions.

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

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

Temperature: 40°C

Detection: ultraviolet-visible spectroscopy (254 nm)

Solvent: tetrahydrofuran

Concentration: 2 mass%

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

[0059]

[Preparation of Block Copolymer: P-2]

(1) 250.0 kg of cyclohexane and 35.0 g of tetrahydrofuran (THF) were charged into a reaction vessel.

(2) 1120 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 4 kg of styrene was added and anionically polymerized. The internal temperature rose to 62°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was raised to 80°C. Thereafter, 53 kg of styrene and 13 kg of 1,3-butadiene were added simultaneously at constant addition rates of 53 kg/h and 13 lg/h, respectively, while maintaining the internal temperature.

(5) After styrene and 1,3-butadiene were completely consumed, the internal temperature of the reaction system was lowered to 75°C and 10 kg of 1,3-butadiene was collectively added to anionically polymerize 1,3-butadiene. The internal temperature rose to 83°C.

(6) After 1,3-butadiene was completely consumed, the internal temperature of the reaction system was lowered to 70°C and 20 kg of styrene was added to anionically polymerize styrene. The polymerization was continued with the reaction heat being removed by cooling the reaction vessel. The internal temperature rose to 90°C.

(7) After styrene was completely consumed, all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing a block copolymer having a polystyrene block, a random block of styrene and butadiene, a polybutadiene block, and a polystyrene block.

(8) The polymerization liquid was preconcentrated and further devolatilized and extruded by a twin-screw extruder with a vacuum vent into pellet form to obtain the block copolymer P-2.

[0060]

[Preparation of Block Copolymer: P-3]

The block copolymer P-3 was obtained in the same manner as P-2, except that 670 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added as the polymerization initiator solution.

[0061]

[Preparation of Block Copolymer: P-4]

The block copolymer P-4 was obtained in the same manner as P-

1, except that 1340 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added as the polymerization initiator solution.

[0062]

[Preparation of Block Copolymer: P-5]

The block copolymer P-5 was obtained in the same manner as P-1, except that 540 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added as the polymerization initiator solution.

[0063]

[Preparation of Block Copolymer: P-6]

(1) 250.0 kg of cyclohexane and 35.0 g of tetrahydrofuran (THF) were charged into a reaction vessel.

(2) 590 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and kept at 30°C.

(3) 20 kg of styrene was added and anionically polymerized. The internal temperature rose to 73°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was lowered to 30°C, and 38 kg of styrene and 42 kg of 1,3-butadiene were added collectively and simultaneously. The internal temperature rose to 100°C.

(5) After styrene and 1,3-butadiene were completely consumed, all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing a block copolymer having a polystyrene block and a tapered block of styrene and butadiene.

(6) The polymerization liquid was preconcentrated and further devolatilized and extruded by a twin-screw extruder with a vacuum vent to obtain the desired pelletized block copolymer (P-6).

[0064]

[Preparation of Block Copolymer: P-7]

(1) 250.0 kg of cyclohexane and 35.0 g of tetrahydrofuran (THF) were charged into a reaction vessel.

(2) 630 mL of a 10 mass% cyclohexane solution of n-butyl lithium was added thereto as a polymerization initiator solution and the kept at 30°C.

(3) 30 kg of styrene was added and anionically polymerized. The internal temperature rose to 79°C.

(4) After styrene was completely consumed, the internal temperature of the reaction system was raised to 80°C. Thereafter, 31 kg of styrene and 9 kg of 1,3-butadiene were added simultaneously at

constant addition rates of 31 kg/h and 9 kg/h, respectively, while maintaining the internal temperature.

(5) After 1,3-butadiene was completely consumed, the internal temperature of the reaction system was lowered to 70°C and 30 kg of styrene was added to anionically polymerize styrene. The polymerization was continued with the reaction heat being removed by cooling the reaction vessel. The internal temperature rose to 93°C.

(6) After styrene was completely consumed, all polymerization active terminals were finally deactivated by water to obtain a polymerization liquid containing a block copolymer having a polystyrene block, a random block of styrene and butadiene, a polybutadiene block, and a polystyrene block.

(7) The polymerization liquid was preconcentrated and further devolatilized and extruded by a twin-screw extruder with a vacuum vent into pellet form to obtain the block copolymer P-7.

The conditions under which the block copolymers P-1 - P-7 were prepared are shown in Table 1.

[0065]

[Table 1]

Table 1		P-1	P-2	P-3	P-4	P-5	P-6	P-7
Cyclohexane	-	kg	250	250	250	250	250	250
THF	-	g	35	35	35	35	35	35
n-Butyl Lithium	-	ml	960	1120	670	1340	540	630
Styrene	-	kg	17	4	4	17	17	20
Styrene	Continuous Addition	kg	-	53	53	-	-	31
1,3-Butadiene		kg	-	13	13	-	-	9
Styrene	Collective Addition	kg	60	-	-	60	38	-
1,3-Butadiene		kg	23	-	-	23	42	-
1,3-Butadiene	-	kg	-	10	10	-	-	-
Styrene	-	kg	-	20	20	-	-	30
Mass Ratio of Vinyl Aromatic Hydrocarbon and Conjugated Diene		mass%	77/23	77/23	77/23	77/23	58/42	91/9
Number Average Molecular Weight		x 10000 g/mol	14.0	12.0	20.0	10.0	25.0	20.0

[0066]

[Preparation of Composition: SBC-A - SBC-I]

Compositions SBC-A - SBC-I were prepared in accordance with the compositions in Table 2, by melt-kneading the copolymers as needed.

[0067]

[Measurement of Melt Mass Flow Rate]

The melt mass flow rates (MFR) of the obtained compositions SBC-A - SBC-I were measured in accordance with JIS K 7210. However, the second resin composition of the non-foamed layer also contains an anti-blocking agent, and its melt mass flow rate is the value measured using a sample prepared by melt-kneading 100 parts by mass of the composition SBC-A, SBC-C, SBC-D, SBC-E, or SBC-F and the anti-blocking material in the prescribed ratio shown in Table 3 and Table 4.

Name of Instrument: No. 120-LABOT melt flow index tester (YASUDA SEIKI SEISAKUSHO, LTD.)

Temperature: 200°C

Load: 5 kg

Die: standard die

[0068]

[Table 2]

Table 2		SBC-A	SBC-B	SBC-C	SBC-D	SBC-E	SBC-F	SBC-G	SBC-H	SBC-I
Composition	kind	P-1	P-2	P-2	P-2	P-3	P-5	P-4	P-6	P-7
	mass%	100	100	67	88	100	100	100	100	100
	kind	-	-	P-3	P-3	-	-	-	-	-
	mass%	-	-	33	12	-	-	-	-	-
Butadiene Ratio	mass%	23	23	23	23	23	23	23	42	9
MFR	g/10 min	5	15	7	13	2	1	20	5	9

[0069]

[Example 1]

Hereinafter, the production method of the heat shrinkable film (heat shrinkable foamed film) of Example 1 will be described.

[0070]

The heat shrinkable foamed film of Example 1 was made by the method described below. For convenience of explanation, the second layer of the heat shrinkable film according to the present embodiment will be described as the front and rear layers (front layer or rear layer when either is represented) and the first layer will be described as the inner layer. The production step of the heat shrinkable foamed film will be explained by being divided into (1) extrusion of the front and rear layers, (2) extrusion of the inner layer, and (3) stretching of the sheet (film).

[0071]

(1) Sheet Extrusion of Front and Rear Layers

The second resin composition, which was obtained by melt-mixing 100 parts by mass of the block copolymer of SBC-A as the front and rear layers with 1.3 parts by mass of "E640N (product name)" (made by TOYO STYRENE Co.,Ltd) as the anti-blocking agent in accordance with the mass ratio shown in Table 3, was extruded into sheet form using an extruder equipped with a multilayer T-die with a lip width of 300 mm, which is capable of extruding and molding a three-layer sheet made of two kinds of materials. The extruder that melts the resin for the front and rear layers and supplies it to the above-mentioned multilayer die was a 40 mm diameter single screw extruder, and the set temperature thereof was 200°C. The set temperature of the multilayer T-die was 190°C.

[0072]

(2) Sheet Extrusion of Inner Layer

The inner layer was co-extruded simultaneously with the extrusion of the front and rear layers described in (1), using the block copolymer of SBC-D (first resin composition) and 0.6 parts by mass of "Polythlene ES405 (product name)" (made by EIWA CHEMICAL IND. CO.,LTD) as the foaming agent master batch (foaming agent MB). Polythlene ES405 contains baking soda, and the amount corresponding to baking soda in 0.6 parts by mass was 0.24 parts by mass. The extruder for the resin for the inner layer was a 65 mm diameter single screw extruder, and the set temperature was 200°C. By using the extruder equipped with a multilayer T-die, the front and rear layers described in (1) and the inner layer described in (2) were discharged from the multilayer T-die as the three-layer laminated sheet made of two kinds of materials in which the front and rear layers and the inner layer adhered to each other. As for the block copolymer of SBC-D, 91 parts by mass of the pellet of the block copolymer P-2 and 9 parts by mass of the pellet of the block copolymer P-3 are in a dry-blended state at the inlet of the extruder, but both pellets are melt-mixed in the extruder and supplied to the multilayer die. The set temperature of the multi-layer T-die was 190°C. The mass ratio of SBC-A (second resin composition) and SBC-D (first resin composition) supplied to the front layer/inner layer/rear layer was 1/2/1. The thickness of the obtained laminated sheet (foamed film) was 0.30 mm, and the thickness ratio of the front layer/inner layer/rear layer was 1/3/1 because foaming occurs in the inner layer.

[0073]

(3) Stretching of Laminated Sheet

The foamed film, which is the obtained laminated sheet, was placed at 80°C in a longitudinal stretching machine having two rolls with different rotation speeds to prevent stretching in the MD direction (i.e., the stretching ratio was 1.0 times), and then placed in a tenter-type lateral stretching machine and stretched by 4.5 times in the TD direction at 90°C to finally obtain the 70 µm-thick heat shrinkable foamed film of Example 1.

[0074]

The films of Examples 2-9 and Comparative Examples 1-5 were made in the same manner as in Example 1, under the conditions described in Tables 3 and 4.

[0075]

<Specific Gravity>

[0076]

The specific gravity of the heat shrinkable foamed film was measured by cutting a test piece from the foamed film and using it in accordance with "measuring method by weighing in liquid" in JIS Z8807:2012, using the instrument shown below.

Name of Instrument: MD-200S (made by Alfa Mirage Co., Ltd.)

The specific gravity was indicated to be sufficiently low when the specific gravity of the heat shrinkable foamed film was within the range indicated by "Excellent", and was judged to be effective to solve the problem of the present invention. Even when the specific gravity was within the range indicated by "Good", it was judged to be at a level that can solve the problem of the present invention. However, when the specific gravity was within the range indicated by "Bad", it was judged that the problem of the present invention cannot be solved.

Excellent: specific gravity < 0.92

Good: $0.92 \leq$ specific gravity < 0.97

Bad: $0.97 \leq$ specific gravity

[0077]

<Surface Roughness>

Three-dimensional surface roughness measurement (i.e., measurement of surface smoothness) in the range of 1 mm × 0.5 mm was performed using "Surfcoder ET4000 (name of instrument)" (made by Kosaka Laboratory Ltd.).

For evaluation, the arithmetic average surface roughness (Ra) was used, which is defined as follows: the roughness curve is obtained by scanning in the MD direction of the film, and the standard length (L) is extracted therefrom in the direction of the average line; the x-axis is taken in the direction of the average line of the extracted part and the y-axis is taken in the direction of the vertical magnification of the extracted part; the absolute value of $f(x)$ is integrated in the range from 0 to L and divided by L when the roughness curve is expressed by $y = f(x)$, thereby defining the arithmetic average surface roughness (Ra).

The measurement results were evaluated using the following criteria. That is, when the arithmetic average surface roughness (Ra) of the heat shrinkable foamed film was within the range indicated by "Excellent", it was judged that the printability on the film surface was not particularly problematic and effective to solve the problem of the present invention. Even when the arithmetic average surface roughness (Ra) was within the range indicated by "Good", it was judged to be at a level that can solve the problem of the present invention. However, when the value of Ra was within the range indicated by "Bad", it was judged that the printing would be hindered and the problem of the present invention cannot be solved.

Excellent : $Ra < 0.3 \mu m$

Good : $0.3 \leq Ra \leq 0.4$

Bad : $0.4 < Ra$

[0078]

<Heat Shrinkage Rate>

The heat shrinkage rate at 100°C was calculated by immersing the stretched film (heat shrinkable foamed film) in warm water adjusted at 100°C for 10 seconds and using the following formula.

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

L1: Length before shrinkage (in the main stretching (TD) direction)

L2: Length after shrinkage (in the main stretching (TD) direction)

The calculated heat shrinkage rate was evaluated in accordance with the following criteria. When the evaluation of the heat shrinkage rate was "Excellent" or "Good", the film was judged to have the basic characteristic of the heat shrinkable film, i.e.,

heat shrinkage rate, and to be not problematic in practical use.

Excellent: $70\% < \text{heat shrinkage rate}$

Good: $60\% \leq \text{heat shrinkage rate} \leq 70\%$

Bad: $\text{heat shrinkage rate} < 60\%$

[0079]

<Separability in Water>

The heat shrinkable foamed film and the PET bottle were cut into 1 cm squares, placed in water, stirred, and allowed to stand for 1 minute. Thereafter, the separation state was evaluated.

Excellent: The foamed film piece and the PET bottle piece were completely separated vertically in water.

Bad: The foamed film piece and the PET bottle piece were not partially or completely separated in water.

[0080]

<Film-forming Property>

The film-forming property was evaluated in accordance with the following criteria. When the evaluation of the film-forming property is "Excellent" or "Good", the heat shrinkable foamed film can be produced.

Excellent: The film-forming property is excellent.

Good: Film formation is possible, but the following problems (*1)-(*3) may occur in the film-forming property.

*1: Foaming is difficult to be stabilized.

*2: FE (fish-eye: generation of foreign matter due to kneading problem or the like) tends to increase.

*3: Breakage may occur.

Bad: Film formation is impossible.

[0081]

[Examples 2-9 and Comparative Examples 1-5]

As with Example 1, the heat shrinkable foamed films of Examples 2-9 and Comparative Examples 1-5 were made in accordance with Tables 3 and 4. The physical properties and the evaluations of the heat-shrinkable foamed films are shown in Tables 3 and 4.

[0082]

[Table 3]

Table 3		Example								
		1	2	3	4	5	6	7	8	9
Non-foamed Layer	Kind of Resin (Second Resin Composition)	SBC-A	SBC-C	SBC-A	SBC-A	SBC-A	SBC-E	SBC-C	SBC-A	SBC-A
	E640N [phr] (Anti-blocking Agent)	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
	MFR [g/10 min]	5	7	5	5	5	2	7	5	5
	Kind of Resin (First Resin Composition)	SBC-D	SBC-C	SBC-B	SBC-D	SBC-D	SBC-D	SBC-D	SBC-H	SBC-I
Foamed Layer	MFR [g/10 min]	13	7	15	13	13	13	13	5	9
	Added Amount of Foaming Agent MB [phr]	0.6	0.6	0.6	0.4	0.8	0.6	0.6	0.6	0.6
	Amount of Foaming Agent (Baking Soda) [phr]	0.24	0.24	0.24	0.16	0.32	0.24	0.24	0.24	0.24
	Ratio of Supplied Resin Amount (Mass) [Front Layer/Inner Layer/Rear Layer]	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1
Constitution of Foamed Film	Layer Thickness Ratio [d1/d2/d3]	1/3/1	1/3/1	1/3/1	1/3/1	1/3.5/1	1/3/1	1/3/1	1/3/1	1/3/1
	Specific Gravity	0.91	0.90	0.95	0.95	0.82	0.92	0.91	0.90	0.91
		Excellent	Excellent	Good	Good	Excellent	Excellent	Excellent	Excellent	Excellent
		0.22	0.40	0.19	0.13	0.38	0.18	0.32	0.40	0.21
Property and Evaluation	Surface Roughness	Excellent	Good	Excellent	Excellent	Good	Excellent	Good	Good	Excellent
		75%	75%	75%	75%	75%	75%	75%	75%	70%
		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good
	Separability in Water	Excellent	Excellent	Good	Good	Excellent	Excellent	Excellent	Excellent	Excellent
Film-forming Property	Excellent	Excellent	Good ^{*1}	Excellent	Excellent	Excellent	Good	Excellent ^{*2}	Good - Excellent ^{*3}	

[0083]

[Table 4]

Table 4		Comparative Example				
		1	2	3	4	5
Non-foamed Layer	Kind of Resin (Second Resin Composition)	SBC-A	SBC-A	SBC-A	SBC-F	SBC-D
	E640N [phr] (Anti-blocking Agent)	1.3	1.3	1.3	1.3	1.3
	MFR [g/10 min]	5	5	5	1	13
Foamed Layer	Kind of Resin (First Resin Composition)	SBC-G	SBC-F	SBC-D	SBC-D	SBC-D
	MFR [g/10 min]	20	1	13	13	13
	Added Amount of Foaming Agent MB [phr]	0.6	0.6	1.2	0.6	0.6
	Amount of Foaming Agent (Baking Soda) [phr]	0.24	0.24	0.48	0.24	0.24
Constitution of Foamed Film	Ratio of Suppled Resin Amount (Mass) [Front Layer/Inner Layer/Rear Layer]	1/2/1	1/2/1	1/2/1	1/2/1	1/2/1
	Layer Thickness Ratio [d1/d2/d3]	1/3/1	1/3.5/1	1/4/1	1/3/1	1/3/1
Property and Evaluation	Specific Gravity	1.00	0.80	0.73	0.91	0.90
		Bad	Excellent	Excellent	Excellent	Excellent
	Surface Roughness	0.02	0.56	0.98	0.40	0.87
		Excellent	Bad	Bad	Good	Bad
	Heat Shrinkage Rate (100°C)	75%	75%	75%	75%	75%
		Excellent	Excellent	Excellent	Excellent	Excellent
	Separability in Water	Bad	Excellent	Excellent	Excellent	Excellent
	Film-forming Property	Good *1	Bad	Excellent	Bad	Excellent

Reference Signs List

[0084]

1: foamed layer

3,4: non-foamed layer

5,6: adhesive layer (undercoat layer)

CLAIMS

1. A foamed film, comprising: a foamed layer; and a non-foamed layer, wherein:

a first resin composition constituting the foamed layer contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit;

a melt mass flow rate of the first resin composition at 200°C under a load of 5 kg is 5.0-15.0 g/10 min;

a second resin composition constituting the non-foamed layer contains one or more kinds of block copolymers having a vinyl aromatic hydrocarbon monomer unit and a conjugated diene monomer unit;

a melt mass flow rate of the second resin composition at 200°C under a load of 5 kg is 2.0-7.0 g/10 min; and

specific gravity of the foamed film is 0.8 or higher and lower than 1.0.

2. The foamed film of Claim 1, wherein the melt mass flow rate of the first resin composition at 200°C under a load of 5 kg is higher than that of the second resin composition at 200°C under a load of 5 kg.

3. The foamed film of Claim 1 or 2, wherein the first resin composition and/or the second resin composition contain(s) 10-40 mass% of the conjugated diene monomer unit when a total of the vinyl aromatic hydrocarbon monomer unit and the conjugated diene monomer unit in each composition is taken as 100 mass%.

4. A heat shrinkable film using the foamed film of any one of Claims 1 to 3.

5. A label using the foamed film of any one of Claims 1 to 3 or the heat shrinkable film of Claim 4.