

SPECIFICATION

TUBULAR MOLDING MATERIAL AND HEAT-SHRINKABLE FILM

TECHNICAL FIELD

[0001] The present invention relates to a tubular molding material, and a heat-shrinkable film using said material.

BACKGROUND ART

[0002] While polyvinyl chlorides have been conventionally used in the heat-shrinkable films for shrink-wrap and the like, the use of block copolymers consisting of vinyl aromatic hydrocarbons and conjugated dienes or resin compositions thereof has become more common in recent years. There are a number of different production methods for such heat-shrinkable films, the simplest of which is a method known as tubular molding.

The production of heat-shrinkable films using the above-mentioned block copolymers consisting of vinyl aromatic hydrocarbons and conjugated dienes or resin compositions thereof is difficult, and Patent Document 1 discloses a method involving strict temperature control of the stretching process in order to stabilize the molding. Furthermore, Patent Document 2 discloses that a certain type of block copolymer consisting of vinyl aromatic hydrocarbons and conjugated dienes is suitable for the tubular molding method.

Patent Document 1: JP S50-6673A

Patent Document 2: JP H07-216186A

[0003] Tubular molding is a method of producing a heat-shrinkable film by

extruding a melted resin from annular die in the form of a tube, appropriately controlling the temperature of the tube, and injecting a gas into the tube to inflate the tube (hereinafter referred to as "bubble forming") and stretch the film in a direction perpendicular to the direction of flow. The force necessary to stretch the film by formation of the tube is obtained by injecting the gas into the tube, resulting in a difference between the pressure inside the tube and the pressure outside the tube.

[0004] A problem with the tubular film forming method is that the film extruded in tubular form from the die is folded by a pinch roller before cooling to room temperature, which can result in blocking between the inner surfaces of the film. This makes it difficult to peel the films apart again, preventing stable film production. Furthermore, stable production can be made even more difficult in film forming equipment that folds the film using a pinch roller at a temperature near the softening point of the resin or even higher temperatures.

[0005] In tubular film formation, the film width is sometimes fixed by bringing the inflated tube into contact with a cooling ring. However, in conventional resin compositions consisting of vinyl aromatic hydrocarbons and conjugated dienes, stable film production is not always possible due to reasons such as poor slidability with respect to the cooling ring.

[0006] Therefore, there has been a demand for the development of a tubular molding material using a resin composition comprising a block copolymer consisting of vinyl aromatic hydrocarbons and conjugated dienes, having both blocking resistance and slidability in order to enable stable film production.

DISCLOSURE OF THE INVENTION

[0007] The present invention has the purpose of offering a tubular molding material having vinyl aromatic hydrocarbons and conjugated dienes as main components, excelling in stability of bubble formation when producing a

heat-shrinkable film, and a heat-shrinkable film using said molding material.

[0008] In other words, the present invention can be summarized as follows.

- (1) A tubular molding material comprising a vinyl aromatic hydrocarbon and a conjugated diene as main components, the tubular molding material comprising (a) a microcrystalline wax having a melting point, as defined by JIS K2235, of 75 °C to 98 °C; and (b) a glyceride wherein the average degree of polymerization of the glycerin backbone is 1-10, and a fatty acid ester group represented by the general formula R-COO- is such that the number of carbon atoms in R is 11-21.
- (2) A tubular molding material in accordance with (1) above, comprising 0.01 to 3 parts by mass of the microcrystalline wax (a) and 0.01 to 3 parts by mass of the glyceride (b).
- (3) A heat-shrinkable film using a tubular molding material in accordance with (1) or (2) above.
- (4) A covering material for use in PET bottles using a heat-shrinkable film in accordance with (3) above.

[0009] By using the tubular molding material of the present invention, the blocking resistance and slidability can be improved, thereby solving the problem of blocking between films occurring due to physical factors such as pressure from nip rollers during production of films.

MODES FOR CARRYING OUT THE INVENTION

[0010] The tubular molding material of the present invention comprises a vinyl aromatic hydrocarbon and a conjugated diene as main components, and must also contain a microcrystalline wax (a) and a glyceride (b).

[0011] In tubular molding, the tubular film is often folded using nip rollers, causing the films to be physically pressed, so that if the tubular molding material being used has a low melting point or if the film is folded by the nip rollers while the film temperature is still high, the films can fuse together and

result in blocking, preventing stable production of high-quality films.

[0012] While this blocking effect can be reduced by raising the temperature of the glass transition point of the tubular molding material, this also has the adverse effect of reducing stretchability, and decreasing the shrinkability at low temperatures. Therefore, in order to achieve good anti-blocking performance without raising the glass transition point of the molding material, a filler or additive having anti-blocking properties must be added.

[0013] Examples of fillers having anti-blocking properties include high-impact polystyrene (HIPS), vinyl aromatic hydrocarbon-(meth)acrylic acid ester and/or (meth)acrylic acid copolymer crosslinked beads, vinyl aromatic hydrocarbon copolymer crosslinked beads, and inorganic beads such as silica beads and quartz beads.

When requiring a film appearance with good transparency, the use of HIPS, vinyl aromatic hydrocarbon-(meth)acrylic acid ester and/or (meth)acrylic acid copolymer crosslinked beads and vinyl aromatic hydrocarbon copolymer crosslinked beads is preferable. The proportional content of these fillers should be no more than 10 parts by mass, preferably 0.05 to 5 parts by mass, and more preferably 0.1 to 3 parts by mass with respect to 100 parts by mass of the block copolymer composition.

[0014] Examples of additives having anti-blocking properties include slip agents, anti-fogging agents and anti-static agents, of which slipping agents are most common. Examples of slip agents include fatty acids, fatty acid esters, fatty acid amides, glycerin fatty acid esters (glycerides), sorbitan fatty acid esters, pentaerythritol fatty acid esters, sucrose fatty acid esters and propylene glycol fatty acid esters, as well as polyolefin waxes such as polyethylene wax and polypropylene, paraffin wax, microcrystalline wax, and petrolatum.

[0015] Since tubular molding involves extrusion of a melted resin from die in the form of a tube followed immediately by folding with nip rollers before adequate cooling, the anti-blocking properties must be achieved immediately

after extrusion, in addition to which subsequent processing involves folding the film by nip rollers in a hot water bath set to the stretching temperature, so that the anti-blocking properties must be achieved at higher temperatures.

Aside from the technique of adding a filler having anti-blocking properties described above, anti-blocking properties can be achieved at high temperatures by using hydrocarbon waxes having high melting points such as polyethylene wax, polypropylene wax, microcrystalline wax, paraffin wax and petrolatum. Polyethylene wax, polypropylene wax and microcrystalline wax are more preferable, and microcrystalline wax is most preferable.

[0016] The melting point of the microcrystalline wax, in accordance with the JIS K2235-5.3.2 standard, should be 75 °C to 98 °C. If the microcrystalline wax has a melting point below 75 °C, the microcrystalline wax can easily move to the film surface, thus degrading the appearance of the film, and lowering the printability of the film. On the other hand, if the microcrystalline wax has a melting point exceeding 98 °C, the speed of movement to the film surface will not be sufficient, so anti-blocking properties cannot be quickly achieved. While there is a method of raising the film temperature to obtain sufficient movement speed, this makes it difficult to achieve stable tube formation.

The above-described JIS K2235-5.3.2 standard corresponds to the ASTM D1321 standard.

[0017] The melting point of the microcrystalline wax in the present invention is measured by the following method.

Equipment: Melting Point Tester (product of Meitech, product name Automatic Wax Melting Point Tester WMP-104)

Test Method: In accordance with JIS K2235-5.3.2, a melt sample was attached to a mercury bulb portion of a melting point measuring thermometer, heated under the defined conditions and the temperature at which the first drop fell from the thermometer was recorded.

[0018] The amount of microcrystalline wax added should be 0.01-3 parts by mass, preferably 0.03 to 1 parts by mass, more preferably 0.1 to 0.3 parts by mass with respect to 100 parts by mass of a block copolymer. If there is less than 0.01 parts by mass of microcrystalline wax, sufficient anti-blocking properties often cannot be achieved. On the other hand, if there is more than 3 parts by mass of microcrystalline wax, the extrusion by the extruder can be unstable.

When using a high melting point hydrocarbon-based wax alone, the movement speed to the film surface cannot be considered to be adequate, and anti-blocking properties sometimes cannot be quickly achieved. In order to obtain high-temperature anti-blocking properties immediately after extrusion of the melted resin, a slip agent with high mobility should also be used.

[0019] The slip agent with high mobility should preferably be chosen from among slip agents with sufficiently low solubility in the tubular molding material. For tubular molding materials having a block copolymer consisting of vinyl aromatic hydrocarbons and conjugated dienes as the main component a slip agent with suitably high hydrophilicity, for example a polyhydric fatty acid ester such as a glycerin fatty acid ester (glyceride), a sorbitan fatty acid ester, a pentaerythritol fatty acid ester or a sucrose fatty acid ester should preferably be used, more preferably a glyceride.

The amount of glyceride added should be 0.01 to 3 parts by mass, preferably 0.03 to 1 parts by mass, more preferably 0.1 to 0.5 parts by mass with respect to 100 parts by mass of the block copolymer. On the other hand, if the glyceride exceeds 3 parts by mass, the extrusion may become unstable.

[0020] The glyceride should be such that in the fatty acid ester groups represented by R-COO-, the number of carbon atoms in R is 11 to 21, preferably 17 to 21.

If R in the glyceride has fewer than 11 carbon atoms, the compatibility with the hydrocarbon-based wax can be reduced, as a result of which the speed

of attainment of the anti-blocking properties from the hydrocarbon-based wax can decrease, as well as making it difficult to provide the tubular molding material with suitable solubility. If there are more than 23, the hydrophilicity can become too low, making it difficult to achieve sufficient slidability with respect to the cooling rings.

[0021] Additionally, the glyceride should be such that the average degree of polymerization of the glycerin backbone is 1 to 10, more preferably 1 to 4.

When the average degree of polymerization of the glycerin backbone exceeds 10, the hydrophilicity can increase too much, making it difficult to provide an appropriate solubility to the tubular molding material having a block copolymer consisting of vinyl aromatic hydrocarbons and conjugated dienes as the main component. While the hydrophilicity of glycerides is commonly indicated by using HLB values, the glycerides used for the tubular molding material of the present invention should preferably have an HLB value of 3 to 16, more preferably 4 to 12. If the HLB value of the glyceride is less than 3, the hydrophilicity can decrease too much, so that sufficient slidability with respect to the cooling ring cannot be obtained. On the other hand, if the HLB value of the glyceride exceeds 16, the compatibility with tubular molding materials can be reduced, making dispersion in the resin difficult.

[0022] Examples of vinyl aromatic hydrocarbons that can be used in the production of 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.

[0023] Examples of conjugated dienes that can be used in the production of 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.

[0024] The block copolymer used in the present invention can be produced by

polymerizing monomers of vinyl aromatic hydrocarbons and conjugated dienes in a dehydrated organic solvent using an organic lithium compound as an initiator, in the presence of a randomizing agent if needed. The organic solvent may be an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane and isooctane, an alicyclic hydrocarbon such as cyclohexane, methylcyclohexane and ethylcyclohexane, or an aromatic hydrocarbon such as benzene, toluene, ethylbenzene and xylene.

[0025] The organic lithium compound is a compound having at least one lithium atom bonded to the molecule, examples of which include monofunctional organic lithium compounds such as ethyllithium, n-propyllithium, n-butyllithium, sec-butyllithium and tert-butyllithium, as well as polyfunctional organic lithium compounds such as hexamethylene dilithium, butadienyl dilithium and isoprenyl dilithium.

[0026] While tetrahydrofuran (THF) is often used as a randomizer, other possibilities include ethers, amines, thioethers, phosphoramides, alkylbenzene sulfonates, and potassium or sodium alkoxides.

Examples of ethers include dimethylether, diethylether, diphenylether, diethylene glycol dimethylether and diethylene glycol dibutylether. Examples of amines include tertiary amines, such as trimethylamine, triethylamine and tetramethylethylene diamine, as well as cyclic amines. Aside therefrom, triphenylphosphine, hexamethylphosphoramide, potassium or sodium alkylbenzene sulfonate, and potassium or sodium butoxide can also be used as randomizers.

[0027] The amount of these randomizers to be added should be no more than 10 parts by mass, preferably 0.001 to 8 parts by mass with respect to 100 parts by mass of the total amount of monomers added. As for the time of addition, it can be before the polymerization reaction begins, or during the polymerization. Additionally, it can be further supplemented as needed.

[0028] The block copolymer solution obtained in this way is treated by adding a

polymerization stopper such as water, alcohol or carbon dioxide in an amount sufficient to inactivate the active terminals, to thereby inactivate the block copolymer. The method for recovering the block copolymer from this block copolymer solution may be any appropriate method, including a method of pouring this solution into a poor solvent medium such as methanol to cause precipitation, a method of evaporating the solvent using heating rollers or the like to cause deposition (drum dryer method), a method of concentrating the solution using a concentrator, then removing the solvent using a vent extruder, and a method of dispersing the solution in water, then blowing steam to heat and eliminate the solvent (steam stripping).

[0029] The tubular molding material of the present invention can use a single block copolymer obtained in this way, or may be a mixture of a plurality of such block copolymers. Alternatively, it can be used in a mixture with another type of polymer such as a vinyl aromatic hydrocarbon polymer, a graft copolymer of a vinyl aromatic hydrocarbon polymer and a conjugated diene, a copolymer of a vinyl aromatic hydrocarbon and a (meth)acrylic acid ester, or a polyolefin. The proportional content should preferably be no more than 30 parts by mass with respect to 100 parts by mass of the block copolymer composition. The method of mixture may be a method of mixing while melting with an extruder, or a method of blending solutions of the respective components, then removing the solvent by one of the methods described above.

[0030] Aside from the slip agents, anti-fogging agents and anti-static agents described above, examples of other additives include mainly heat stabilizers and weather resistance agents. Examples of heat stabilizers include phenolic anti-oxidants 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 and n-octadecyl-3-(4-hydroxy-3,5-di-tert-butylphenyl)propionate, and phosphorus-based antioxidants such as 2,2'-methylene

bis(4,6-di-tert-butylphenyl)octylphosphite and
tris(2,4-di-tert-butylphenyl)phosphite.

[0031] Examples of weather resistance agents include benzotriazole UV
absorbers such as
2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole and hindered
amine
weather resistance agents such as
tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane
tetracarboxylate. White oil and silicone oil can also be added.

[0032] These additives should preferably contained in an amount of no more
than 5 parts by mass of the block copolymer composition.

[0033] The heat-shrinkable film using the tubular molding material of the
present invention is preferably used for heat-shrinkable labels and
heat-shrinkable cap seals, and may also be applied to packaging films and the
like.

While the tubular molding material and heat-shrinkable film using said
material according to the present invention have been described above, these
represent only possible embodiments of the present invention, and the present
invention should not be construed as being limited thereto.

EXAMPLES

[0034] Herebelow, the present invention shall be described in detail with
reference to examples, but the present invention is not to be construed as being
limited by these examples.

[0035] [Reference Example 1]

- (1) 490 kg of cyclohexane were loaded into a reaction vessel.
- (2) 35.7 kg of styrene monomer were added, then 1600 ml of n-butyllithium
(10 mass% cyclohexane solution) were added while stirring at an internal
temperature of 30 °C to allow polymerization.

(3) The internal temperature was lowered to 40 °C, 69.3 kg of styrene monomer and 8.9 kg of butadiene monomer were added at once, then the result was allowed to adequately polymerize.

(4) The internal temperature was adjusted to 60 °C, 69.3 kg of styrene and 26.8 kg of butadiene were added at once, and the polymerization was completed.

[0036] [Reference Example 2]

(1) 500 kg of cyclohexane were loaded into a reaction vessel.

(2) 8.0 kg of styrene monomer were added, then 1280 ml of n-butyllithium (10 mass% cyclohexane solution) were added while stirring at an internal temperature of 30 °C to allow polymerization.

(3) A total of 110.0 kg of styrene monomer and a total of 13.4 kg of butadiene monomer were simultaneously added at a constant addition rate of respectively 87.8 kg/h and 10.7 kg/h while maintaining an internal temperature of 80 °C, and the state was maintained for an adequate time after the addition was completed.

(4) After the butadiene gas was completely consumed, 18.6 kg of butadiene were added at once at an internal temperature of 75 °C, and polymerization was allowed to continue.

(5) 50.0 kg of styrene monomer were further added at once, and the polymerization was completed.

[0037] [Reference Example 3]

(1) 500 kg of cyclohexane were loaded into a reaction vessel.

(2) 4.0 kg of styrene monomer were added, then 1950 ml of n-butyllithium (10 mass% cyclohexane solution) were added while stirring at an internal temperature of 30 °C to allow polymerization.

(3) A total of 119.0 kg of styrene monomer and a total of 11.8 kg of butadiene monomer were simultaneously added at a constant addition rate of respectively 100.8 kg/h and 10.0 kg/h while maintaining an internal temperature

of 80 °C, and the state was maintained for an adequate time after the addition was completed.

(4) After the butadiene gas was completely consumed, 36.4 kg of butadiene were added at once at an internal temperature of 70 °C, and polymerization was allowed to continue.

(5) 28.8 kg of styrene monomer were further added at once, and the polymerization was completed.

[0038] The characteristics of block copolymers of Reference Examples 1-3 obtained in this way are shown in Table 1. In the table, A represents polystyrene blocks, B represents polybutadiene blocks, C represents random blocks and D represents tapered blocks.

[0039] [Table 1]

	Reference Example 1	Reference Example 2	Reference Example 3
Structure of block copolymer	A-D-D	A-C-B-A	A-C-B-A
Wt.-avg. mol. wt. of block copolymer	200,000	200,000	140,000
St/Bd (mass% ratio)	83/17	84/16	76/24

[0040] The block copolymers of Reference Examples 1-3 were mixed at a ratio of Reference Example 1/Reference Example 2/Reference Example 3 = 33.3 mass%/33.3 mass%/33.4 mass% to form a mixed resin composition. Then, the slip agents were added to the 100 parts by mass of the mixed resin composition in the amount shown in Tables 2 to 4. Then, a uniaxial extruder was used to melt-knead the composition at 200 °C, to obtain tubular molding materials according to Examples 1-11 and Comparative Examples 1-8. The melting points of the microcrystalline waxes were measured in compliance with the method described in JIS K2235-5.3.2.

[0041] [Table 2]

	Example										
	1	2	3	4	5	6	7	8	9	10	11
Melting point of microcrystalline wax (°C)	75	75	83	83	93	93	98	98	98	98	93
Amount of microcrystalline wax added (parts by mass)	0.1	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.1	1	0.1
Avg. polymerization of glycerin backbone in glyceride (-)	1	2	1	4	1	2	1	2	4	1	10
No. of carbons in R of (R-COO-) of fatty acid ester in glyceride	17	17	21	17	17	17	21	17	17	17	7
HLB of glyceride	4.3	5.7	4.2	5.6	4.3	5.7	4.2	5.7	5.6	5.4	12
Amount of glyceride added (parts by mass)	0.1	0.5	0.1	0.1	0.1	0.1	0.1	0.1	0.2	1	0.1

[0042] [Table 3]

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Melting point of microcrystalline wax (°C)	67	-	93	93
Amount of microcrystalline wax added (parts by mass)	0.1	0	0.1	0.1
Avg. polymerization of glycerin backbone in glyceride (-)	1	1	-	11<
No. of carbons in R of (R-COO-) of fatty acid ester in glyceride	21	17	-	7
HLB of glyceride	4.2	4.3	-	16.4
Amount of glyceride added (parts by mass)	0.1	0.1	0	0.1

[0043] [Table 4]

	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Type of slip agent used	fatty acid amide	fatty acid ester	polyolefin oxide	silicone oil
Chemical name	erucic acid amide	partially saponified montanic acid	polyethylene oxide wax	methylphenyl polysiloxa

		ester		ne
Product name	Alflow P-10	Licowax OP	Licowax PED 521	KF54
Manufacturer	NOF Corp.	Clariant Japan	Clariant Japan	Shin-Etsu Chemical
Amount of slip agent added (parts by mass)	0.3	0.3	0.3	0.3
Melting point of microcrystalline wax (°C)	-	93	83	67
Amount of microcrystalline wax added (parts by mass)	0	0.1	0.3	0.5

[0044] The tubular molding materials of the examples and comparative examples shown in Tables 5 and 6 were subjected to film forming tests according to the methods described below, using a common stretch preheat type tubular film forming machine (manufactured by Yi-Chen, model MCE-50) having a water tank, its state was observed, and the resulting heat-shrinkable film was also evaluated in accordance with the method described below. The results are shown in Tables 5 and 6.

[0045] (1) The tubular molding materials of the proportional contents indicated in Tables 5 and 6 were loaded into an extruder, melt-kneaded at 200 °C for adequate plasticization, then extruded in the form of a tube. Next, a gas was injected into the tubes and the tubes were cooled from the outside by suitably blowing to stably inflate the tubes to an appropriate tube diameter.

(2) The tubes were folded by nip rollers positioned at an appropriate height above the die, and the spacing between the die, screw rotation speed and nip roller speed were adjusted to obtain a film with an average thickness of about 0.1 mm. The pressure from the nip rollers was adjusted to the least necessary for the gas in a first stage of the tube from leaking past the nip rollers.

(3) The films were collected after being folded by the nip rollers, and the blocking between the films was evaluated in accordance with the standards described below.

[0046] (A) Tube Inner Surface Separation Strength Test

Using the direction of flow of the tubes (hereinafter abbreviated to "MD direction") and the direction perpendicular to the tubes (hereinafter abbreviated to "TD direction") as standards, the collected tubes were cut into samples 15 mm long in the MD direction and 15 cm long in the TD direction. Next, a marker line was drawn at a location 4 cm from an end of each sample in the TD direction. Using this as the boundary line, the films on the shorter side were peeled apart, and the peeled films were respectively folded by 90° at the boundary line to form a T-shaped sample. These were set in a Tensilon Tensile Testing Machine RTC-1210 manufactured by A&D Company, by anchoring the peeled ends of the films with a chuck, and the separation strength [N] when pulled at a tensile speed of 200 mm/min was measured. The measurements 15 to 60 seconds after initial application of tension were averaged, and the same operation was repeated ten times to compute the average value Z [N].

[0047] (4) After passing through the nip rollers, the film was passed through a tank filled with hot water at 85 °C to perform stretch preheating, and gas was injected to inflate the film and form a bubble until adequate contact was made with a cooling ring (hereinafter referred to as a sizing ring) for fixing the size of the tube in the radial direction so as to obtain an appropriate tube diameter (this operation shall be referred to hereinafter as "sizing"). The bubble formation stability was evaluated in accordance with the following standards.

[0048] (B) Gas Injectability

In order to evaluate "gas injectability", the state of the surface of the inner surfaces of the tubes after injection of gas was judged by eye, and evaluated according to the following criteria.

Good (Gd): The inner surfaces of the tube are easily peeled apart by injection of gas.

Fair (Fr): The inner surfaces of the tube are peeled apart by injection of gas, but there is some resistance and noise is made when the inner surfaces of the tube come apart, or there are

unstable vibrations.

Poor (Pr): The inner surfaces of the tube are blocked together so that the film is torn when inflated, or the film is completely blocked, so that gas injection cannot be performed.

[0049] (C) Slidability with Sizing Ring

In order to evaluate "slidability with the sizing ring", the slidability between the film and the sizing ring during injection of gas until achieving adequate contact between the outer surface of the tube and the sizing ring was judged by eye, and evaluated according to the following criteria.

Good (Gd): The sliding between the tube and the sizing ring is stable and there is no noise due to catching.

Fair (Fr): During sliding between the tube and the sizing ring, there is some noise due to catching and the movement is unstable.

Poor (Pr): The tube is caught by the sizing ring, resulting in considerable deformation or tearing of the tube.

[0050] (5) The film was extracted after bubble formation to obtain a heat-shrinkable film.

(D) Measurement of Heat Shrinkage Rate

The heat shrinkage rate of the heat-shrinkable film was measured by the following method.

(1) Samples 100 mm long in the MD direction and 100 mm long in the TD direction were cut out from the stretched film.

(2) These samples were immersed in hot water at 100 °C for 10 seconds, immediately water-cooled, then the water was wiped off and the lengths L (mm) of the samples in the MD and TD directions were measured.

(3) The heat-shrinkage rates were calculated by the following formula.

$$\text{Heat Shrinkage Rate (\%)} = \{(100.0 - L)/100.0\} \times 100$$

[0051] [Table 5]

	Examples										
	1	2	3	4	5	6	7	8	9	10	11

(I) Separation strength average A(N) over 10 measurements $\times 100$	6.6	5.3	6.0	6.0	4.5	4.7	4.6	4.8	4.8	5.0	5.1
(II) Gas injectability when stretching second stage tube	G d	G d	Fr	Fr	G d	G d	G d	G d	G d	G d	G d
(III) Slidability w/ sizing ring when stretching second stage tube	G d	G d	G d	G d	G d	G d	G d	G d	G d	G d	G d
(IV) TD heat shrinkage rate (%) of resulting film	48.7	49.1	47.3	47.1	48.5	48.5	49.0	46.7	47.8	47.6	47.3
(V) MD heat shrinkage rate (%) of resulting film	9.8	11.3	10.2	9.9	10.0	9.7	10.5	9.5	9.9	10.1	10.4

[0052] [Table 6]

	Comparative Examples							
	1	2	3	4	5	6	7	8
(I) Separation strength average A(N) over 10 measurements $\times 100$	10.9	20.3	13.6	25.9	50.7	51.5	44.1	13.8
(II) Gas injectability when stretching second stage tube	Fr	Pr	Fr	Pr	Pr	Pr	Pr	Fr
(III) Slidability w/ sizing ring when stretching second stage tube	Pr	NT	Pr	NT	NT	NT	NT	Pr
(IV) TD heat shrinkage rate (%) of resulting film	43.7	NT	41.7	NT	NT	NT	NT	43.2
(V) MD heat shrinkage rate (%) of resulting film	13.4	NT	20.3	NT	NT	NT	NT	16.1

NT = not testable

[0053] The results of Tables 5 and 6 show that the tubular molding material of the present invention is such that even when the films are pressed together by nip rollers at a high temperature, the films do not block together and can be easily separated, so bubble formation during tubular film formation remains

stable, enabling a heat-shrinkable film excelling in heat shrinking ability to be obtained.

[0054] On the other hand, Comparative Examples 1-4 containing microcrystalline waxes and glycerides having structures other than those claimed by the present invention, and Comparative Examples 5-8 containing different types of slip agents did not provide blocking resistance between the films and slidability with respect to the sizing ring, and thus lacked stability in bubble formation and did not yield films of good quality.

Furthermore, those in which the amounts of the microcrystalline wax or glyceride exceeded the claimed ranges were extremely lacking in extrusion stability, while those in which the amounts were less than the claimed ranges provided almost no blocking resistance effects or slidability with respect to the sizing ring, and were not suitable for stable film production.

INDUSTRIAL APPLICABILITY

[0055] As described above, the tubular molding material of the present invention is a material suitable for production of heat-shrinkable films by tubular molding, and the films using this material may be applied to bottle labels, cap seals and the like. Furthermore, aside from tubular film formation methods, the tubular molding material of the present invention can be used favorably in various other applications requiring blocking resistance at high temperatures.

CLAIMS

- [1] A tubular molding material comprising a vinyl aromatic hydrocarbon and a conjugated diene as main components, the tubular molding material comprising:
- (a) a microcrystalline wax having a melting point, as defined by JIS K2235, of 75 °C to 98 °C; and
 - (b) a glyceride wherein the average degree of polymerization of the glycerin backbone is 1-10, and a fatty acid ester group represented by the general formula R-COO- is such that the number of carbon atoms in R is 11-21.
- [2] A tubular molding material in accordance with claim 1, comprising 0.01 to 3 parts by mass of the microcrystalline wax (a) and 0.01 to 3 parts by mass of the glyceride (b).
- [3] A heat-shrinkable film using a tubular molding material in accordance with claim 1 or 2.
- [4] A covering material for use in PET bottles using a heat-shrinkable film in accordance with claim 3.