

Description

Title of Invention: WRAP FILM AND WRAP FILM ROLL

Technical Field

[0001]

The present invention relates to a wrap film and a wrap film roll comprising the same.

Background Art

[0002]

Wrap films have heretofore been used for foods, etc. in many general households because the wrap films are excellent in characteristics such as adhesion between films or to adherends, gas barrier properties for gases such as water vapor or oxygen, and cuttability for use in being placed in presentation boxes. The wrap films for household use are mainly used as overlays to preserve foods in refrigerators or freezers or to heat foods placed in containers in microwave ovens.

[0003]

Among current commercially available products of such wrap films for household use, films composed mainly of polyvinylidene chloride resin are regarded as being most convenient. Meanwhile, other films or the like composed mainly of polyethylene resin, polypropylene resin, polyvinyl chloride resin or poly-4-methylpentene-1

resin, etc. are also commercially available. However, all of these films fall far short of the adhesion of the polyvinylidene chloride resin wrap films and are inferior in aptitude for plastic wraps. Thus, plastic wraps made of polyvinylidene chloride are widely prevalent.

[0004]

For example, Patent Documents 1 and 2 disclose a technique relating to a property of being resistant to splitting in the machine direction of a film as well as a property of being easy to cut in the width direction.

[0005]

Patent Document 3 discloses a technique of improving adhesion or oxygen and/or water vapor barrier properties upon vapor deposition of a metal or a metal oxide, through a surface fibril structure.

List of Prior Art Documents

Patent Document

[0006]

Patent Document 1: Japanese Patent No. 5501791

Patent Document 2: International Publication No. WO
2016/189987

Patent Document 3: Japanese Patent Laid-Open No. 11-
077824

Summary of Invention

Problems to be Solved by Invention

[0007]

The aptitude for plastic wraps of wrap films for household use requires rigidity, etc. in addition to transparency and cuttability. Such wrap films for household use are also required to have stability with less melting to make holes and severe deformation, cling to containers or degradation of the films themselves even during cooking in microwave ovens or the like, and required to have wrap film strength after heating so as not to mix fragments of the wrap films into foods due to the tearing of the wrap films when the plastic wraps are peeled off after cooking. The wrap films for household use are further required to have adhesion between plastic wraps and to containers at the time of wrapping. Consumers have a strong desire for, in addition to the adhesion, favorable pullout properties, which are characteristics inconsistent with the adhesion, when a rolled wrap film in a presentation box is pulled out of the box. On the assumption that consumers employ the wrap films for household use, the wrap films in 1000 m or longer rolls of webs are rewound around paper cores or the like into a roll length on the order of several tens of m. In this step of rewinding the wrap films around paper cores or the like (rewinding step), the films tear if having insufficient film strength. Such films cannot be transported, possibly incurring reduction in production efficiency.

[0008]

Nevertheless, none of Patent Documents 1 to 3 can attain a wrap film that sufficiently possesses all of a splitting suppressive effect at the time of cutting, a wind-back suppressive effect, oxygen and water barrier properties, a tearing suppressive effect after heating to a high temperature, a tearing suppressive effect at the time of rewinding around a paper core, adhesion, rigidity and transparency.

[0009]

An object of the present invention is to provide a novel wrap film having favorable aptitude for plastic wraps, the wrap film having favorable adhesion in use, having rigidity, transparency, an anti-splitting effect and an anti-wind-back effect, being resistant to tearing even after heating at a high temperature (e.g., in a microwave oven), having a low incidence of tearing at the time of rewinding, and being excellent in oxygen and water barrier properties.

Means for Solving Problems

[0010]

The present inventors have conducted diligent studies from the viewpoint of having adhesion in use, rigidity, transparency, an anti-splitting effect and an anti-wind-back effect, being resistant to tearing even after heating at a high temperature (e.g., in a microwave

oven), having a low incidence of tearing at the time of rewinding, and being excellent in oxygen and water barrier properties. As a result, the present inventors have found that the object can be attained by having a tensile strength, a tensile elongation and a tensile modulus in specific ranges, and also found that such characteristics are effective for retaining sufficient breaking strength, particularly, when a subject is pulled in the TD direction, and suppressing tearing at the time of rewinding, reaching the present invention. Specifically, the present invention relates to the following.

(1)

A wrap film which has a tensile strength of 100 MPa or larger, a tensile elongation of 100% or less, and a tensile modulus of 280 MPa or larger in the transverse direction (TD), and

and which has a tensile modulus of 380 MPa or larger in the machine direction (MD).

(2)

The wrap film according to (1), wherein the wrap film has a crystal long period of 12.5 nm or smaller.

(3)

The wrap film according to (1) or (2), wherein as for a thermal shrinkage at 120°C measured in conformity with ASTM D-2732, the thermal shrinkage in the machine direction (MD) is 4 to 30%, and a ratio of the thermal

shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is 2 or less.

(4)

The wrap film according to any of (1) to (3), wherein the wrap film has a network structure that is observed in an atomic force microscope phase image on the surface of at least one layer, wherein a network of the network structure is constituted by fibrils, and an average width of the fibrils observed in the network structure is 145 nm or smaller.

(5)

The wrap film according to any of (1) to (4), wherein the wrap film has an oxygen transmission rate equal to or lower than $110 \text{ cm}^3/\text{m}^2\cdot\text{day}\cdot\text{atm}$ at 23°C , and a water vapor transmission rate equal to or lower than $20 \text{ g}/\text{m}^2\cdot\text{day}$ at 38°C and 90% RH.

(6)

The wrap film according to any of (1) to (5), wherein the wrap film has a thickness of 5 to $15 \text{ }\mu\text{m}$.

(7)

The wrap film according to any of (1) to (6), wherein the wrap film comprises a copolymer containing 85 to 97% by mass of a vinylidene chloride monomer and 15 to 3% by mass of a vinyl chloride monomer.

(8)

A method for producing the wrap film according to any of (1) to (7), comprising a step of drawing an undrawn sheet in the machine direction and the transverse direction, wherein a draw ratio in the machine direction is 4.0 or less, and a draw ratio in the transverse direction is 5.8 or more.

(9)

A roll comprising the wrap film according to any of (1) to (7) wound around a core.

Advantages of Invention

[0011]

The present invention can provide a novel wrap film having favorable aptitude for plastic wraps, the wrap film having favorable adhesion in use, having rigidity, transparency, an anti-splitting effect and an anti-wind-back effect, being resistant to tearing even after heating in a microwave oven, having a low incidence of tearing at the time of rewinding, and being excellent in oxygen and water barrier properties.

Brief Description of Drawings

[0012]

[Figure 1] Figure 1 is a schematic view showing a network structure that is observed in an atomic force microscope (AFM) phase image.

[Figure 2] Figure 2 shows an atomic force microscope (AFM) phase image of the wrap film surface in Example 1 of the present application.

[Figure 3] Figure 3 shows an atomic force microscope (AFM) phase image of the wrap film surface in Comparative Example 1 of the present application.

[Figure 4] Figure 4 is a diagrammatic view showing one example of a method for producing the wrap film of the present embodiment.

Mode for Carrying Out Invention

[0013]

Hereinafter, the mode for carrying out the present invention (hereinafter, referred to as the "present embodiment") will be described in detail. The present invention is not limited by embodiments given below and can be carried out through various changes or modifications without departing from the spirit of the present invention.

[0014]

The wrap film of the present embodiment has tensile strength X_1 (MPa) of 100 or larger, preferably in the range of $100 \leq X_1 \leq 300$, in the transverse direction (hereinafter, also referred to as the "TD direction"). The tensile strength in the range of 100 MPa or larger in the TD direction offers sufficient breaking strength along a direction perpendicular to the TD direction upon

cutting, and in the case of a rolled plastic wrap for food packaging, curbs splitting problems upon cutting. The tensile strength in the range of 300 MPa or smaller in the TD direction does not increase too much breaking strength along a direction perpendicular to the TD direction upon cutting, and in the case of a rolled plastic wrap for food packaging, tends to curb splitting problems upon cutting. The tensile strength in the TD direction is more preferably $170 \leq X_1 \leq 300$, still more preferably $190 \leq X_1 \leq 300$, in terms of practical usability.

[0015]

The wrap film of the present embodiment has tensile elongation X_2 (%) of 100 or less, preferably $15 \leq X_2 \leq 100$, in the TD direction. The tensile elongation in the range of 100% or less in the TD direction facilitates cutting the film, and in the case of a rolled plastic wrap for food packaging, curbs splitting problems upon cutting. The tensile elongation in the range of 15% or more in the TD direction facilitates cutting the film because of moderate stretch, and in the case of a rolled plastic wrap for food packaging, tends to curb splitting problems upon cutting. The tensile elongation in the TD direction is more preferably $15 \leq X_2 \leq 60$, still more preferably $15 \leq X_2 \leq 50$, in terms of practical usability.

[0016]

The wrap film of the present embodiment has tensile modulus X_3 (MPa) of $380 \leq X_3$, preferably $380 \leq X_3 \leq 900$, in the machine direction (hereinafter, also referred to as the "MD direction") and tensile modulus Y (MPa) of $280 \leq Y$, preferably $280 \leq Y \leq 880$, in the TD direction. The tensile modulus in the range of 380 MPa or larger in the MD direction improves the rigidity of the film and facilitates its handling. The tensile modulus in the range of 280 MPa or larger in the TD direction improves the rigidity of the film and facilitates its handling. The tensile modulus in the range of 900 MPa or smaller in the MD direction renders the film moderately hard and tends to facilitate its handling. The tensile modulus in the range of 880 MPa or smaller in the TD direction renders the film moderately hard and tends to facilitate its handling. The tensile modulus in the MD direction is more preferably $540 \leq X_3 \leq 900$, still more preferably $620 \leq X_3 \leq 900$, in terms of practical usability. Likewise, the tensile modulus in the TD direction is more preferably $420 \leq Y \leq 880$, still more preferably $500 \leq Y \leq 880$, in terms of practical usability. Examples of the method for controlling the tensile strength, the tensile elongation and the tensile modulus in the TD direction, and the tensile modulus in the MD direction in the ranges described above include, but are not particularly limited to, a method of adjusting a draw ratio to 4.0 or less (preferably 3.8 or less) in the machine direction and to

5.8 or more in the transverse direction, a method of using a polymer having a low glass transition temperature, and a method of appropriately adding a nucleating agent.

[0017]

In the present embodiment, the tensile strength, the tensile elongation and the tensile modulus in the TD direction, and the tensile modulus in the MD direction can be measured by a method described in Examples mentioned later.

[0018]

As for a thermal shrinkage at 120°C measured in conformity with ASTM D-2732, the thermal shrinkage in the machine direction (MD) of the wrap film of the present embodiment is 4 to 30%, and the ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is 2 or less. The wrap film of the present embodiment having a thermal shrinkage thus controlled in the specific range retains sufficient strength, particularly, even after heating at a high temperature, and can curb tearing problems after heating to a high temperature.

[0019]

The thermal shrinkage in the machine direction (MD) of the wrap film of the present embodiment at 120°C is more preferably 4% to 25%, still more preferably 4% to 20%, in terms of practical usability.

[0020]

In the present embodiment, the MD and TD thermal shrinkages at 120°C can be measured by a method described in Examples mentioned later.

[0021]

[Constituent of wrap film]

The wrap film of the present embodiment is preferably formed from a constituent containing a polymer.

[0022]

In the present embodiment, the polymer is a polymer having the ability to form a film. This polymer means a polymer that occupies 50% by weight or more of the whole film.

[0023]

Amorphous polymers cannot form a surface network structure (which will be mentioned later) effective for conferring adhesion. It is therefore preferred that such an amorphous polymer should not be used as the polymer of which the film of the present embodiment is composed mainly.

[0024]

However, even an amorphous polymer may be blended, for use, in an amount that allows a crystalline polymer to be partially crystallized. The crystalline polymer may be a hydrogen bonding polymer, such as cellulose or aromatic polyamide, which has no clear crystalline

melting point. However, a crystalline polymer having a crystalline melting point equal to or higher than the temperature of its decomposition is operationally disadvantageous because this crystalline polymer causes wet film formation to be attempted and requires steps such as the recovery of a solvent. Thus, a polymer that has a crystalline melting point of 350°C or lower and is melt-moldable in a production process is suitably used from the viewpoint of operability.

[0025]

Polyvinylidene chloride resin, polyolefin resin, polyester resin or polyamide resin is suitably used as the polymer constituting the wrap film of the present embodiment. Examples of the polyolefin resin can include polyethylene, polypropylene, polybutene-1, poly-4-methylpentene-1 and copolymers composed mainly of these resins. Examples of the polyester resin can include polyethylene terephthalate, polypropylene terephthalate, poly-1,4-cyclohexanedimethylene terephthalate, polyethylene-2,6-naphthalate, polylactic acid and polyhydroxyglycolic acid. Examples of the polyamide resin can include nylon 6, nylon 7, nylon 66, nylon 610, nylon 612, nylon 46 and nylon 6T.

[0026]

A polyvinylidene chloride resin composition is more suitably contained as the polymer constituting the wrap film of the present embodiment. The polyvinylidene

chloride resin composition may be a homopolymer of a vinylidene chloride monomer or may be a copolymer of a vinylidene chloride monomer and a monomer copolymerizable therewith. In the present specification, the polyvinylidene chloride resin wrap film refers to a wrap film comprising a polyvinylidene chloride resin composition. The polyvinylidene chloride resin composition may contain one type of polyvinylidene chloride resin or may contain two or more types of polyvinylidene chloride resins.

[0027]

Examples of the monomer copolymerizable with the vinylidene chloride monomer include, but are not particularly limited to, vinyl chloride, acrylic acid esters such as methyl acrylate and butyl acrylate, methacrylic acid esters such as methyl methacrylate and butyl methacrylate, acrylonitrile and vinyl acetate. Among them, vinyl chloride is preferred from the viewpoint of easy-to-balance between oxygen and water barrier properties and extrudability, and excellent film adhesion. These monomers may each be used alone or may be used in combination of two or more thereof.

[0028]

In the case of using a copolymer of a vinylidene chloride monomer and the monomer described above, the copolymer preferably consists of 85 to 97% by mass of the vinylidene chloride monomer and 15 to 3% by mass of the

monomer copolymerizable therewith from the viewpoint of crystallinity, processability and film physical properties, etc. The vinylidene chloride monomer with a proportion of 85% by mass or more can further improve oxygen and water barrier properties and film cuttability. The vinylidene chloride monomer with a proportion of 97% by mass or less can further improve processability. The proportions of the monomers are values calculated from the integration ratios of respective monomer component-derived peaks in ^1H -NMR spectra measured with FX-270 (manufactured by JEOL Ltd.) using d-THF as a solvent.

[0029]

The weight-average molecular weight of the polyvinylidene chloride resin composition is not particularly limited and is preferably 70,000 to 110,000, more preferably 80,000 to 100,000. The polyvinylidene chloride resin composition having a weight-average molecular weight equal to or larger than the lower limit value described above can produce more favorable film strength. The weight-average molecular weight equal to or smaller than the upper limit value described above can further improve processability. In this context, the weight-average molecular weight is measured by gel permeation chromatography (GPC) using tetrahydrofuran as a mobile phase and is a value calibrated with polystyrene having a known molecular weight.

[0030]

The polyvinylidene chloride resin composition can be supplemented with an additive known in the art such as a plasticizer or a stabilizer. The plasticizer is not particularly limited, and a plasticizer known in the art may be used. Examples thereof include acetyl tributyl citrate, acetylated monoglyceride and dibutyl sebacate. The stabilizer is not particularly limited, and a stabilizer known in the art may be used. Examples thereof include epoxidized plant oils such as epoxidized soybean oil and epoxidized flaxseed oil.

[0031]

In addition, a weather resistance improving agent, an anti-fogging agent, an antimicrobial agent, an oligomer such as polyester, a polymer such as MBS (methyl methacrylate-butadiene-styrene) or the like known in the art for use in food packaging materials may be added thereto without inhibiting the advantages of the present embodiment. The weather resistance improving agent is not particularly limited, and a weather resistance improving agent known in the art may be used. Examples thereof include ultraviolet absorbers such as 2-(2'-hydroxy-3'5'-di-tert-butylphenyl)-5-chlorobenzotriazole. The anti-fogging agent is not particularly limited, and an anti-fogging agent known in the art may be used. Examples thereof include surfactants such as glycerin fatty acid ester, diglycerin fatty acid ester and sorbitan fatty acid ester. The antimicrobial agent is

not particularly limited, and an antimicrobial agent known in the art can be used. Examples thereof include natural product-derived antimicrobial agents such as grapefruit seed extracts and moso bamboo extracts.

[0032]

The wrap film of the present embodiment is not necessarily required to have single composition of one layer. In the case of a multilayer structure, practical adhesion does not vary as long as a layer that comes into contact with a container is composed mainly of a crystalline polymer, has a network structure that is observed in an AFM phase image, and contains a liquid component. The wrap film of the present embodiment may have a multilayer structure of two or more layers.

[0033]

The wrap film of the present embodiment may comprise a liquid component.

[0034]

The liquid component suitably used differs depending on the type of the polymer. As at least one type of liquid component, for example, a liquid component containing an alkyl group or a methylene segment is suitably used for an aliphatic hydrocarbon polymer, and a liquid component containing a functional group having hydrogen bonding ability, such as a carbonyl group, an ether group or a hydroxy group is suitably used for an

ester polymer or an amide polymer, from the viewpoint of imparting flexibility to the film.

[0035]

Examples of the liquid component having an alkyl group include mineral oil, liquid paraffine and saturated hydrocarbon compounds. Examples of the liquid component containing a functional group having hydrogen bonding ability, such as a carbonyl group, an ether group or a hydroxy group can include aliphatic alcohols, alicyclic alcohols, their polyhydric alcohols, and esters of these alcohol components and aliphatic or aromatic (polyvalent) carboxylic acids, esters of aliphatic hydroxycarboxylic acids and alcohols and/or fatty acids, and modified products of these esters, and polyoxyethylene alkyl ethers and esters thereof. More specific examples thereof include glycerin, polyglycerins such as diglycerin, triglycerin and tetraglycerin, mono-, di- and triesters and polyesters of these (poly)glycerins used as starting materials of alcohol components with acid components such as fatty acids, for example, lauric acid, palmitic acid, stearic acid, oleic acid or linoleic acid, esters of sorbitan and these fatty acids, esters of ethylene glycol, propylene glycol, tetramethylene glycol and their condensates with the fatty acids, esters of aliphatic hydroxycarboxylic acids such as citric acid, malic acid or tartaric acid and lower alcohols having 10 or less carbon atoms, esters of polyvalent carboxylic

acids such as malonic acid, succinic acid, glutaric acid or adipic acid and aliphatic alcohols, and modified products of these esters, such as epoxidized soybean oil and epoxidized flaxseed oil. Particularly, in the case of using the wrap film of the present embodiment as a plastic wrap for food packaging, a liquid component which is a food additive stipulated in the Food Sanitation Law is suitably used. A liquid component having a boiling point of 200°C or higher is suitably used from the viewpoint of heat resistance.

[0036]

[Surface structure of wrap film]

The wrap film of the present embodiment preferably has a network structure that is observed in an atomic force microscope (hereinafter, also referred to as "AFM") phase image on the surface of at least one layer.

[0037]

In the wrap film of the present embodiment, it is preferred for the network structure that the average width of fibrils constituting the network that is observed in an AFM phase image should be 145 nm or smaller. The average width of the fibrils of 145 nm or smaller renders film strength moderate and improves cuttability. This improved cuttability also decreases the incidence of wind-back and decreases the incidence of tearing at the time of rewinding. Since a developed crystal structure is formed after drawing, the thermal

shrinkage in the machine direction (MD) is reduced.

Thus, the ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is also reduced.

[0038]

The average width of the fibrils is preferably 1 nm or larger because: the network structure sufficiently retains an additive on the surface; the adhesion is moderate; and pullout properties are also improved. The average width of the fibrils is more preferably 10 nm to 145 nm, still more preferably 45 nm to 145 nm, in terms of practical usability.

[0039]

In this context, the AFM phase image is an image of information on a phase with respect to the stimulus of an AFM cantilever. In the wrap film of the present embodiment, the network structure is, for example, a portion where the fibrils have less retardation in the phase with respect to the stimulus of a cantilever, while a pore is a portion with large retardation in the phase. As illustrated in Figure 1, the dark portions are pores, and the bright portions are fibrils. Specifically, when the fibrils and the pores are compared, the pore portions are more amorphous.

[0040]

In the present embodiment, the average width of the fibrils can be measured by a method described in Examples mentioned later.

[0041]

For the wrap film of the present embodiment, various formation methods may be used as a method for forming the surface network structure. The network structure can be formed, for example, by oriented crystallization in a biaxial drawing process. For developing the network structure in the wrap film of the present embodiment, it is preferred to form the network structure mentioned above by biaxial drawing. However, in the case of wet film formation or the like, the polymer is substantially drawn by contraction stress through a step such as desolvation under strain without aggressive drawing. Therefore, aggressive biaxial drawing does not have to be performed unless free contraction occurs.

[0042]

As for the timing of drawing, when the crystallization rate of the polymer is fast, this polymer may be melt-extruded, cooled in air, and drawn while crystallized. In the case of time-consuming crystallization, drawing in a melted state may not be followed by the crystallization. Thus, the polymer does not undergo effective oriented crystallization and may not develop the network structure. It is therefore preferred that the polymer should be temporarily

solidified and then drawn at a temperature equal to or higher than the glass transition temperature. A nucleating agent may be appropriately added thereto in order to accelerate the crystallization rate.

[0043]

[Crystal long period of wrap film]

The wrap film of the present embodiment preferably has a crystal long period of 12.5 nm or smaller, more preferably 8.2 nm to 12.5 nm. The crystal long period of 8.2 nm or larger allows the film to have sufficient strength upon cutting, and in the case of a rolled plastic wrap for food packaging, reduces splitting problems upon cutting. Such sufficient strength of the film also decreases the incidence of tearing at the time of rewinding. Since a developed crystal structure is formed after drawing, the thermal shrinkage in the machine direction (MD) is reduced. Thus, the ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is also reduced.

[0044]

On the other hand, the crystal long period of 12.5 nm or smaller facilitates cutting the film, and in the case of a rolled plastic wrap for food packaging, reduces splitting problems upon cutting. Such easy cutting of the film also decreases the incidence of tearing at the time of rewinding. Since a developed crystal structure

is formed after drawing, the thermal shrinkage in the machine direction (MD) is reduced. Thus, the ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is also reduced. The crystal long period is still more preferably 9.0 nm to 12.5 nm in terms of practical usability.

[0045]

In the present embodiment, the crystal long period can be measured by a method described in Examples mentioned later.

[0046]

[Evaluation of oxygen and water barrier properties]

In general, plastic wraps are required to have oxygen barrier properties and water barrier properties for preserving freshness.

[0047]

The wrap film of the present embodiment preferably has an oxygen transmission rate equal to or lower than $110 \text{ cm}^3/\text{m}^2\cdot\text{day}\cdot\text{atm}$ at 23°C , and preferably has a water vapor transmission rate equal to or lower than $20 \text{ g}/\text{m}^2\cdot\text{day}$ at 38°C and 90% RH.

[0048]

The wrap film of the present embodiment more preferably has oxygen transmission rate X ($\text{cm}^3/\text{m}^2\cdot\text{day}\cdot\text{atm}$ at 23°C) in the range of $1 \leq X \leq 110$. The oxygen transmission rate in the range of $1 \leq X \leq 110$ offers

sufficient oxygen barrier properties and sufficiently preserves the freshness of foods. $X < 1$ may be less likely to exert sufficient freshness preserving performance. $X > 110$ tends to be less likely to exert sufficient barrier properties. The oxygen transmission rate is still more preferably $1 \leq X \leq 77$, further preferably $1 \leq X \leq 50$, in terms of practical usability. The wrap film of the present embodiment more preferably has water vapor transmission rate Y (g/m²·day at 38°C and 90% RH) in the range of $1 \leq Y \leq 20$. The water vapor transmission rate in the range of $1 \leq Y \leq 20$ offers sufficient water vapor barrier properties and sufficiently preserves the freshness of foods. $Y < 1$ may be less likely to exert sufficient freshness preserving performance. $Y > 20$ tends to be less likely to exert sufficient barrier properties. The water vapor transmission rate is still more preferably $1 \leq Y \leq 18$, further preferably $1 \leq Y \leq 10$, in terms of practical usability.

[0049]

Examples of the method for controlling the oxygen transmission rate and the water vapor transmission rate in the ranges described above include, but are not particularly limited to, a method of adjusting a draw ratio to 4.0 or less (preferably 3.8 or less) in the machine direction and to 5.8 or more in the transverse direction, a method of using a polymer having a low glass

transition temperature, and a method of appropriately adding a nucleating agent.

[0050]

In the present embodiment, the oxygen transmission rate and the water vapor transmission rate can be measured by a method described in Examples mentioned later.

[0051]

[Method for producing wrap film]

Next, one example of a method for producing the wrap film of the present embodiment will be described. Various methods can be adopted to the method for producing the wrap film comprising a polyvinylidene chloride resin composition. An inflation film forming method is usually employed. Specifically, according to the present embodiment, the wrap film can be prepared by inflation molding. More preferably, the wrap film of the present embodiment is a polyvinylidene chloride resin wrap film obtained by drawing the polyvinylidene chloride resin composition described above at least in the MD direction, followed by inflation molding. In the inflation film forming method, for example, the polyvinylidene chloride resin composition is melt-extruded into a tubular form from an annular die. Then, the outer side of the tubular resin is brought into contact with a coolant such as cold water with which a reservoir called cool bath is filled. In this operation,

a coolant such as mineral oil is injected and reserved in the inside of the tubular resin held between the die mouth and pinch rolls, and in this state, the inner side is brought into contact with the coolant for solidification to form a film. In the present specification, this portion of the tubular resin (extrudate) held between the die mouth and pinch rolls is referred to as a "sock". The coolant (liquid) to be injected to the inside of this sock is referred to as a "sock liquid". The sock is folded back with the pinch rolls or the like to form a tubular double-ply film. This double-ply film is referred to as a "parison".

[0052]

Hereinafter, the inflation film forming method will be described more specifically. Figure 4 is a diagrammatic view showing one example of the method for producing the wrap film of the present embodiment.

[0053]

In an extrusion step, a melted polyvinylidene chloride resin composition is first extruded into a tubular form from a die mouth (3) of an annular die (2) using an extruder (1) to form a sock (tubular polyvinylidene chloride resin composition) (4).

[0054]

In a cooling and solidification step, the outer side of the sock (4) which is an extrudate is then brought into contact with cold water in a cool bath (6). A sock

liquid (5) is injected and reserved in the inside of the sock (4) by a routine method so that the sock (4) is cooled from within and without and solidified. In this operation, the sock (4) is in a state where the inner side thereof is coated with the sock liquid (5). The solidified sock (4) is folded back by first pinch rolls (7) to form a parison (8) which is a double-ply sheet. The amount of the sock liquid applied is controlled by the pinch pressure of the first pinch rolls (7).

[0055]

For example, water, mineral oil, an alcohol, a polyhydric alcohol such as propylene glycol or glycerin, or an aqueous solution of cellulose or polyvinyl alcohol can be used as the sock liquid. These sock liquids may be used alone, or two or more types thereof may be used in combination. The sock liquid may be supplemented with the weather resistance improving agent, the anti-fogging agent, the antimicrobial agent or the like described above for use in food packaging materials without inhibiting the advantages of the present embodiment.

[0056]

The amount of the sock liquid applied is not particularly limited and is preferably 50 to 20000 ppm, more preferably 100 to 15000 ppm, still more preferably 150 to 10000 ppm, from the viewpoint of the openability of the parison and the adhesion of the film. In this context, the amount of the sock liked applied (ppm)

refers to the mass of the sock liquid applied to the sock, indicated by mass ppm, based on the total mass of the sock.

[0057]

Subsequently, air is injected to the inner side of the parison (8) so that the parison (8) is reopened into a tubular form. The parison (8) is reheated to a temperature suitable for drawing by warm water (not shown). Warm water attached to the outer side of the parison (8) is squeezed out by second pinch rolls (9). In an inflation step, air is subsequently injected into the tubular parison (8) heated to a suitable temperature. The parison (8) is inflated and drawn into a bubble (10) to obtain a drawn film.

[0058]

The crystal long period of the wrap film can be controlled by a draw ratio or the crystallinity of the polymer constituting the wrap film. The crystal long period tends to be larger as the draw ratio in the TD direction is larger than the draw ratio in the MD direction. The crystal long period tends to be larger as the crystallinity of the polymer is higher.

[0059]

The method for producing the wrap film of the present embodiment preferably comprises the step of drawing an undrawn sheet in the machine direction and the transverse direction. In this case, the draw ratio in

the TD direction is preferably 5.8 or more, and the draw ratio in the MD direction is preferably 4.0 or less. The draw ratio in the MD direction is more preferably larger than 3.4 and 3.8 or less from the viewpoint of film formability. The upper limit of the draw ratio in the TD direction is not particularly limited and is, for example, 8.5 or less.

[0060]

The method for controlling the draw ratio is not particularly limited, and a method known in the art can be employed. Examples thereof include a method of controlling a drawing temperature by changing a warm water temperature for reheating. For decreasing the draw ratio, a lower drawing temperature is more preferred because the inflated bubble is stabilized in a low-draw ratio condition. In this respect, the drawing temperature is preferably higher than drawing room temperature from the viewpoint of the stability of the inflated bubble. The drawing temperature is more preferably 34°C or lower, still more preferably 25°C to 34°C. The drawing temperature is measured at the midpoint of the distance in the MD direction between the point where drawing in the MD direction and the TD direction is completed and the point where winding starts.

[0061]

Then, the drawn film is folded back by third pinch rolls (11) to form a double-ply film (12). The double-ply film (12) is wound around a wind-up roll (13). This film is slit and peeled off so as to form a single-ply film (single peel). Finally, this film is wound around a core such as a paper core to obtain a roll of a wrap film wound around a paper core.

[0062]

The crystal long period is influenced not only by the draw ratio but by a heat history. When the wrap film receives a heat history, the crystal long period is decreased. Thus, tear strength tends to be reduced. Hence, it is preferred that the wrap film should not receive an excessive heat history. In various environments, for example, not only in the case of performing aging treatment but in the case of transporting the wrap film in summer or placing the wrap film near a heat source such as a stove in use in households, it is preferred that the film should not receive a high heat history. This can prevent the crystal long period from being too low and can prevent the film from tearing easily.

[0063]

The method for producing the wrap film of the present embodiment is described above as one example and may be performed using various apparatus configurations,

conditions, etc. other than those described above. For example, other methods known in the art may be employed.

[0064]

[Roll]

The wrap film of the present embodiment can be used in various forms and can be prepared as, for example, a polyvinylidene chloride resin wrap film in a roll form. The wrap film in a roll form may or may not have a core.

[0065]

A form wound around a core can be a wrap film roll comprising, for example, a cylindrical core and the polyvinylidene chloride resin wrap film of the present embodiment wound around the core. The roll refers to an article having a scroll shape in which the wrap film is wound around a core or the like.

[0066]

The wrap film of the present embodiment can effectively curb wind-back problems that arise in the wrap film in a roll form or the like in use. The core is not particularly limited by its material, size, etc., and a core known in the art such as a paper core can be used. The wrap film in a roll form may or may not have a core. The wrap film roll of the present embodiment can be stored, for use, in a presentation box having a cutting blade for cutting the wrap film.

[0067]

[Thickness of wrap film]

The thickness of the wrap film of the present embodiment is not particularly limited and is preferably 5 to 30 μm , more preferably 5 to 15 μm , from the viewpoint of usability and optical characteristics.

[0068]

[Evaluation of adhesion]

The wrap film of the present embodiment has adhesion workload X ($\text{mJ}/25\text{ cm}^2$) in the range of $1 \leq X \leq 2.5$. $1 \leq X$ tends to allow the wrap film to exert sufficient adhesion. $X \leq 2.5$ facilitates peeling off the wrap film and can suppress so-called excessive adhesion, and in the case of a rolled plastic wrap for food packaging, tends to facilitate pull-out. The adhesion workload is more preferably $1.5 \leq X \leq 2.4$, still more preferably $1.8 \leq X \leq 2.3$, in terms of practical usability.

[0069]

[Evaluation of resistance to tearing after hearing]

The wrap film produced by the procedures described above has been drawn in the transverse direction (TD) at a higher ratio than that in the machine direction (MD), and has been drawn in the transverse direction (TD) and the machine direction (MD) within a range that can secure film formation stability. Therefore, the thermal shrinkage in the machine direction (MD) can be adjusted to 4% to 30% at 120°C , and the ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) can be

adjusted to 2 or less. The wrap film having such thermal shrinkage characteristics can be prevented from being broken and mixing its fragments into foods when a container containing contents such as oil and fat foods is overlaid in close contact with the wrap film, which is then exposed to a high temperature by heating in a microwave oven or the like and then peeled off. The thermal shrinkage in the machine direction (MD) at 120°C of the wrap film of the present embodiment is more preferably 4% to 25%, still more preferably 4% to 20%, in terms of practical usability.

Examples

[0070]

Hereinafter, the present invention will be described in more detail with reference to Examples and Comparative Examples. The following measurement methods were used for observing the surface network structure of the wrap film under AFM and for evaluating the wrap film for its crystal long period, tear strength, percentage of splitting problems, adhesion, tensile strength, tensile elongation, tensile modulus, rigidity, transparency, percentage of wind-back, oxygen transmission rate, water vapor transmission rate, thermal shrinkage, resistance to tearing after heating, and incidence of tearing at the time of rewinding.

[0071]

(1) AFM measurement

The film was attached and fixed to a Si wafer. A phase image of the surface was observed under Dimension Icon manufactured by Bruker on the tapping mode. The measurement was carried out using a single-crystal Si cantilever (spring constant (cataloged value): 40 N/m) under conditions involving a scan rate of 0.5 to 2 Hz, a scan size of $1\ \mu\text{m} \times 1\ \mu\text{m}$, and 512×256 or 512×512 sampling points. The tactile pressure of the cantilever was controlled by the film. The set point was in the range of 240 to 320 mV when the target amplitude was 400 mV, and was in the range of 450 to 500 mV when the target amplitude was 800 mV. For fibril width (fibril diameter) measurement, each phase image was divided into quarters. Seemingly typical fibrils of 5 locations were selected for each region. An average value of particularly large fibril diameters from the 5 locations was adopted as the average width of the fibrils.

[0072]

(2) Crystal long period measurement

The crystal long period was determined by small-angle X-ray scattering (SAXS) measurement using the following apparatus and conditions.

Apparatus: NANOPIX manufactured by Rigaku Corp.

X-ray incident direction: film normal direction

X-ray wavelength: 0.154 nm

Optical system: point collimation (1st: 0.55 mm Φ , 2nd:
open, guard: 0.35 mm Φ)

Detector: HyPix-6000 (two-dimensional detector)

Camera length: SAXS: 1113 mm

Light exposure time: Comparative Examples 5 to 8, 10 and
12: 10 min/sample

Examples 1 to 9 and Comparative

Examples 1 to 4, 9 and 11: 1 hr/sample

An X-ray scattering pattern obtained from HyPix-6000
was corrected for the background of the detector and
scattering from an empty cell. Then, the data was
circularly averaged to obtain SAXS profile I (q). The
SAXS profile I (q) was further multiplied by q^2 for
Lorentz correction. Bragg angle θ was calculated
according to (expression 1) from the amplitude of the
scattering vector of a crystal long period-derived peak
of the SAXS profile thus Lorentz-corrected. This value
was substituted into the Bragg equation (expression 2) to
calculate crystal long period d.

[0073]

$$q = 4\pi \sin\theta/\lambda \dots (\text{Expression 1})$$

θ : Bragg angle

q: Amplitude of the scattering vector

λ : X-ray wavelength

[0074]

$$2d \sin\theta = \lambda \dots (\text{Expression 2})$$

d: crystal long period

θ : Bragg angle

λ : X-ray wavelength

[0075]

(3) Tear strength

The tear strength was measured in conformity with ASTM-D-1992. The measurement was performed at 23°C in a 50% RH atmosphere. The tear strength was measured (unit: cN) in the MD direction and the TD direction using Light Load Type Tearing Tester (manufactured by Toyo Seiki Seisaku-sho Ltd.).

[0076]

(4) Percentage of splitting problems

A cut test was conducted using a commercially available wrap film presentation box (manufactured by Asahi Kasei Home Products Corp., trade name: Presentation Box for Saran Wrap(R), 30 cm × 20 m). The test was conducted at 23°C in a 50% RH atmosphere. The film was cut with a presentation box opening fixed to 30°. The probability (%) of splitting of the film when the film thus cut was pulled out was calculated (N = 500) (unit: %).

[0077]

(5) Adhesion

On the assumption that the wrap film would be used in households, the adhesion between wrap films was evaluated. The measurement was performed at 23°C in a 50% RH atmosphere. Two aluminum jigs having a base area

of 25 cm², a height of 55 mm and a weight of 400 g were first provided. A filter paper having the same area as the base area was attached to the undersurface of each of the jigs. The undersurface on which the filter paper was attached to each of the jigs was overlaid with the wrap film without being wrinkled, and fixed with rubber bands. The two jigs were combined such that their undersurfaces overlaid with the wrap film overlapped with each other. The jigs were pressure-bonded under a load of 500 g for 1 minute. Subsequently, both the wrap film-overlaid surfaces were peeled off from each other in a vertical fashion at a rate of 5 mm/min using a tensile compression tester (manufactured by Shimadzu Corp.). The workload necessary for this peeling was measured (unit: mJ/25 cm²).

[0078]

(6) Tensile strength and tensile elongation

The tensile strength and the tensile elongation were measured in conformity with ASTM-D-882. The measurement was performed at 23°C in a 50% RH atmosphere. The wrap film set to a width of 1 cm and an inter-chuck distance of 10 cm was pulled up and down at a rate of 300 mm/min using a tensile compression tester (manufactured by Shimadzu Corp.). The strength (unit: MPa) and the elongation (unit: %) at break were measured.

[0079]

(7) Tensile modulus

The tensile modulus was measured in conformity with ASTM-D-882. The film was cut into a length of 12 cm and a width of 1 cm in the MD direction of the film, and a direction parallel to the TD direction to prepare a measurement sample. The measurement was performed at 23°C in a 50% RH atmosphere. The wrap film set to an inter-chuck distance of 10 cm was pulled up and down at a rate of 5 mm/min using a tensile compression tester (manufactured by Shimadzu Corp.). The strength at 2% displacement (stroke: 2 mm) was multiplied by 50 and thereby converted to that at 100% displacement to measure the tensile modulus (unit: MPa).

[0080]

(8) Evaluation of rigidity

Twenty skilled panelists were provided. A glass container having an opening diameter of 15 cm and a wrap film having both a length and a width of 30 cm were used. The wrap film was evaluated according to the following criteria in consideration of its usability in covering the container.

[0081]

Description of symbols for evaluation

A: The wrap film was excellent in rigidity and was very easy to handle.

B: The wrap film had good rigidity and was handled without problems.

C: The wrap film had poor rigidity, but was handled without problems.

D: The wrap film had poor rigidity and was difficult to use.

[0082]

(9) Haze

The haze was measured in conformity with JIS-K-7136. The measurement was performed at 23°C in a 50% RH atmosphere. The haze was measured (unit: %) using a turbidimeter (manufactured by Nippon Denshoku Industries Co., Ltd.).

[0083]

(10) Evaluation of incidence of tearing at time of rewinding

The double-ply film was slit and peeled off so as to form a single-ply film. Then, the film was wound around a paper core using a commercially available wrap film paper core (manufactured by Asahi Kasei Home Products Corp., trade name: Paper Core for Saran Wrap, 30 cm × 20 m). The winding was performed at a film transportation rate of 300 m/min and a roll length of 20 m. The probability (%) that the film tore during the winding operation and became no longer able to be transported was calculated (N = 3000) (unit: %). The incidence of tearing was evaluated according to the following criteria.

[0084]

Description of symbols for evaluation

A: The incidence of tearing at the time of rewinding was 0.03% or less (the number of tears: 1 or less/3000 runs).

B: The incidence of tearing at the time of rewinding was higher than 0.03% and 0.07% or less (the number of tears: more than 1 and 2 or less/3000 runs).

C: The incidence of tearing at the time of rewinding was higher than 0.07% and 0.10% or less (the number of tears: more than 2 and 3 or less/3000 runs).

D: The incidence of tearing at the time of rewinding was higher than 0.10% (the number of tears: more than 3/3000 runs).

[0085]

(11) Thermal shrinkage

The thermal shrinkage was measured in conformity with ASTM D-2732. For the measurement, a sample of the wrap film was left standing for 1 minute in a thermostat bath adjusted to a set temperature (120°C). After a lapse of 1 minute, the wrap film was taken out of the thermostat bath. The length of a mark placed beforehand was measured in the machine direction (MD) and the transverse direction (TD) within 30 minutes at 23°C in a 50% RH atmosphere. In this respect, the value of decrease from the original length of 10 cm was determined in percentage as a ratio to the original length of 10 cm. This determined percentage serves as the thermal shrinkage.

[0086]

(12) Evaluation of resistance to tearing after heating at 120°C

On the assumption that the wrap film would be used in a microwave oven, the wrap film was evaluated for its resistance to tearing upon heating. The wrap film wound around a paper core was unwound. The film was cut into a length of 10 cm and a width of 10 cm in the MD direction and a direction parallel to the TD direction to prepare an evaluation sample. An incision was made on the end face on the unwinding side (side closer to the surface layer), of the end faces parallel to the TD direction of the cut sample. In order to make the incision, the roll was placed such that the end face on the unwinding side was unwound from the upper direction when an evaluator viewed the wrap film wound around a paper core from the front. This incision was made with a length of 1 cm at an angle of 45° formed by the end faces parallel to the TD direction from a position moved by $1/\sqrt{2}$ cm from the center in a direction of the evaluator's left side. The sample of the wrap film with the incision made by the procedures mentioned above was left standing for 1 minute in a thermostat bath adjusted to a set temperature (120°C). After a lapse of 1 minute, the wrap film was taken out of the thermostat bath and evaluated for its resistance to tearing at 23°C in a 50% RH atmosphere. For the evaluation of the resistance to tearing, the

center of the incised end face among the end faces of the wrap film with the incision made by the procedures mentioned above was weighted to measure a withstand load. The weight started at 10 g and was suspended in order from lightest to heaviest (20 g, 30 g, 40 g, 50 g, 60 g and 70 g). The maximum load when the wrap film tore was measured. The wrap film was more resistant to tearing after heating at a high temperature as the maximum load when the wrap film tore was heavier. The test was conducted at N = 500. An average value from the 500 runs was calculated. The wrap film was evaluated for its resistance to tearing after heating at a high temperature according to the following criteria.

[0087]

Description of symbols for evaluation

A: The average maximum load upon tearing was heavier than 60 g.

B: The average maximum load upon tearing was heavier than 50 g and 60 g or less.

C: The average maximum load upon tearing was heavier than 40 g and 50 g or less.

D: The average maximum load upon tearing was 40 g or less.

[0088]

(13) Oxygen transmission rate

The oxygen transmission rate was measured according to the measurement method of ASTM D 3985 using OX TRAN

2/21MH <trade name> manufactured by MOCON, Inc. A sample was loaded in the apparatus, and a value obtained 4 hours later was employed. The measurement was performed under conditions of 23°C. A smaller oxygen transmission rate means higher oxygen barrier properties.

[0089]

(14) Water vapor transmission rate

The water vapor transmission rate was measured according to the measurement method of ASTM F 1249 using PERMATRAN W-398 <trade name> manufactured by MOCON, Inc. A sample was loaded in the apparatus, and a value obtained 3 hours later was employed. The measurement was performed under conditions of 38°C and 90% RH. A smaller water vapor transmission rate means higher water barrier properties.

[0090]

(15) Percentage of wind-back

A cut test was conducted using a commercially available wrap film presentation box (manufactured by Asahi Kasei Home Products Corp., trade name: Presentation Box for Saran Wrap, 30 cm × 20 m). The test was conducted at 23°C in a 50% RH atmosphere. The film was cut with a presentation box opening fixed to 30°. The probability (%) of wind-back of the film when the film thus cut was pulled out was calculated (N = 500) (unit: %).

[0091]

[Example 1]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) and having a weight-average molecular weight of 90,000 was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film. The weight-average molecular weight was measured by gel permeation chromatography (GPC) using tetrahydrofuran as a mobile phase and was a value calibrated with polystyrene having a known molecular weight.

In this operation, the draw ratio in the MD direction was set to 3.8, and the draw ratio in the TD direction was set to 5.8. The drawing temperature was set to 26°C. This tubular film was folded back, wound, then slit with a width of 300 mm, and wound by 20 m around a paper core having an outside diameter of 36.6 mm and a length of 305 mm while peeled off into a single-ply film, to produce an approximately 10 µm thick wrap film wound around a paper core.

The obtained film was evaluated for its AFM measurement, SAXS measurement, tear strength, tensile elongation, tensile modulus, thermal shrinkage, resistance to tearing after heating at 120°C, incidence of tearing at the time of rewinding, percentage of wind-back, oxygen transmission rate, moisture transmission

rate, adhesion and transparency. The results are shown in Table 1.

[0092]

[Example 2]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.6, and the draw ratio in the TD direction was set to 6.0. The drawing temperature was set to 25°C. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0093]

[Example 3]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.5, and the draw ratio in the TD direction was set to 6.1. The drawing temperature was set to 25°C. An

approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0094]

[Example 4]

A crystalline polymer (85 parts by weight of polylactic acid) serving as a main component, and a liquid component (15 parts by weight of glycerin diacetate monolaurate) were mixed and melted at a temperature of 220°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.8, and the draw ratio in the TD direction was set to 8.0. The drawing temperature was set to 33°C. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0095]

[Example 5]

A crystalline polymer (80 parts by weight of nylon 66) serving as a main component, a liquid component (15 parts by weight of glycerin triacetate), and other

additives (3 parts by weight of epoxidized flaxseed oil and 2 parts by weight of mineral oil) were mixed and melted at a temperature of 280°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.4, and the draw ratio in the TD direction was set to 8.5. The drawing temperature was set to 25°C. An approximately 10 µm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0096]

[Example 6]

A crystalline polymer (80 parts by weight of polypropylene) serving as a main component, a liquid component (10 parts by weight of mineral oil), and other additives (5 parts by weight of MARUKAREZ(R) R and 5 parts by weight of TUFTEC(R) R) were mixed and melted at a temperature of 200°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.8, and the draw ratio in the TD direction was set to 7.2. The drawing temperature was set to 26°C. An approximately 10 µm thick wrap film wound around a paper

core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0097]

[Example 7]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.7, and the draw ratio in the TD direction was set to 5.8. The drawing temperature was set to 25°C. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0098]

[Example 8]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.6, and the draw ratio in the TD direction was set to 6.1. The drawing temperature was set to 34°C. An approximately 10 µm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0099]

[Example 9]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.5, and the draw ratio in the TD direction was set to 6.2. The drawing temperature was set to 31°C. An approximately 10 µm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 1.

[0100]

[Comparative Example 1]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 91/9

(mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 3.7, and the draw ratio in the TD direction was set to 4.3. The drawing temperature was set to 40°C. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0101]

[Comparative Example 2]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 5.0, and the draw ratio in the TD direction was set to 6.0. The drawing temperature was set to 35°C. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0102]

[Comparative Example 3]

Polyethylene was melted at a temperature of 170°C and melt-extruded in a melt extruder. The obtained parison was inflated and drawn into a tubular film.

The draw ratio in the MD direction was set to 5.0, and the draw ratio in the TD direction was set to 5.0. The drawing temperature was set to 39°C. An approximately 10 µm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0103]

[Comparative Example 4]

A crystalline polymer (80 parts by weight of polypropylene) serving as a main component, a liquid component (10 parts by weight of mineral oil), and other additives (5 parts by weight of MARUKAREZ(R) R and 5 parts by weight of TUFTEC(R) R) were mixed and melted at a temperature of 200°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 2.0 × 2.0 using a stretcher while passed through a heating zone set to 140°C, followed by winding. An approximately 10 µm thick wrap film wound

around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0104]

[Comparative Example 5]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 1.0 × 8.6 using a stretcher while passed through a heating zone set to 140°C, followed by winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0105]

[Comparative Example 6]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of

170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 4.3×1.0 using a stretcher while passed through a heating zone set to 38°C, followed by winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0106]

[Comparative Example 7]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 5.3×1.0 using a stretcher while passed through a heating zone set to 39°C, followed by winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0107]

[Comparative Example 8]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 6.3 × 1.0 using a stretcher while passed through a heating zone set to 40°C, followed by winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0108]

[Comparative Example 9]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 8.0×1.0 using a stretcher while passed through a heating zone set to 42°C , followed by winding. An approximately $10\text{ }\mu\text{m}$ thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0109]

[Comparative Example 10]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C , extruded from an extruder equipped with a T die having a slit width of $20\text{ mm} \times 0.5\text{ mm}$, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 3.5×10.0 using a stretcher while passed through a heating zone set to 49°C , followed by winding. An approximately $10\text{ }\mu\text{m}$ thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0110]

[Comparative Example 11]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 5.0 × 7.0 using a stretcher while passed through a heating zone set to 49°C, followed by winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0111]

[Comparative Example 12]

A polyvinylidene chloride resin composition having a vinylidene chloride (VDC)/vinyl chloride (VC) = 88/12 (mass ratio) was mixed and melted at a temperature of 170°C, extruded from an extruder equipped with a T die having a slit width of 20 mm × 0.5 mm, and rapidly cooled in water to form a film-like sheet.

Subsequently, this web was sequentially biaxially drawn at a ratio of 5.0 × 10.0 using a stretcher while passed through a heating zone set to 53°C, followed by

winding. An approximately 10 μm thick wrap film wound around a paper core was produced by an operation conforming to Example 1 except for the conditions described above.

Results of evaluating the obtained film are shown in Table 2.

[0112]

[Table 1]

	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6		Example 7		Example 8		Example 9	
	Present	A	Present	A	Present	B	Present	C	Present	A	Present	A	Present	B	Present	B	Present	A
Draw ratio	3.8	3.6	3.6	3.6	3.5	3.5	3.8	3.8	3.4	3.4	3.8	3.8	3.7	3.7	3.6	3.6	3.5	3.5
	5.8	6.0	6.0	6.0	6.1	6.1	8.0	8.0	8.5	8.5	7.2	7.2	5.8	5.8	6.1	6.1	6.2	6.2
	0.7	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6
Drawing temperature (°C)	26	25	25	25	25	25	33	33	25	25	26	26	25	25	34	34	31	31
Incidence of tearing at time of rewinding																		
Network structure																		
Fibril diameter (nm)	Average value		Present		Present		Present		Present		Present		Present		Present		Present	
	Standard deviation		21.1		29.4		8.6		108.3		143.1		27.5		32.6		52.2	
Tear strength (cN)	0.7	2.7	2.7	2.7	2.4	2.4	0.2	0.2	1.8	1.8	2.1	2.1	2.6	2.6	3.6	3.6	5.4	5.4
	3.7	5.4	5.4	5.4	2.3	2.3	8.2	8.2	9.6	9.6	11.5	11.5	6.5	6.5	5.8	5.8	7.5	7.5
	2.7	2.7	2.7	2.7	1.9	1.9	6.4	6.4	7.0	7.0	8.8	8.8	6.2	6.2	6.8	6.8	5.2	5.2
Percentage of splitting problems (%)	1.4	2.0	2.0	2.0	1.2	1.2	1.3	1.3	1.4	1.4	1.3	1.3	1.0	1.0	0.9	0.9	1.4	1.4
	0	16	16	16	20	20	15	15	12	12	15	15	20	20	20	20	16	16
	23.0	18.0	18.0	18.0	19.7	19.7	28.1	28.1	8.0	8.0	7.0	7.0	24.9	24.9	23.2	23.2	29.4	29.4
Thermal shrinkage (%) 120°C, 1 min	18.0	15.1	15.1	15.1	17.4	17.4	25.1	25.1	5.0	5.0	5.0	5.0	18.5	18.5	17.1	17.1	24.3	24.3
	1.3	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.6	1.6	1.4	1.4	1.3	1.3	1.4	1.4	1.2	1.2
	B	A	A	A	A	A	C	C	A	A	A	A	B	B	B	B	C	C
Resistance to tearing after heating at 120°C																		
Rigidity	B	A	A	A	A	A	A	A	A	A	A	A	C	C	C	C	A	A
Thickness (μm)	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
Adhesion workload (mJ/25cm ²)																		
Tensile strength (MPa)	1.7	1.7	1.7	1.7	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.7	1.7	1.7	1.7	1.9	1.9
	115.8	122.6	122.6	122.6	160.0	160.0	217.8	217.8	286.8	286.8	320.1	320.1	116.4	116.4	137.9	137.9	208.5	208.5
	193.0	171.0	171.0	171.0	174.0	174.0	213.5	213.5	234.6	234.6	291.0	291.0	127.5	127.5	142.6	142.6	192.5	192.5
Tensile elongation (%)	0.6	0.7	0.7	0.7	0.9	0.9	1.0	1.0	1.2	1.2	1.1	1.1	0.9	0.9	1.0	1.0	1.1	1.1
	65.9	60.1	60.1	60.1	69.0	69.0	46.3	46.3	23.4	23.4	18.9	18.9	64.9	64.9	61.0	61.0	48.0	48.0
	50.0	59.0	59.0	59.0	64.0	64.0	42.1	42.1	23.0	23.0	17.2	17.2	81.1	81.1	74.1	74.1	51.2	51.2
Modulus (MPa)	1.3	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.0	1.0	1.1	1.1	0.8	0.8	0.8	0.8	0.9	0.9
	422.3	623.0	623.0	623.0	540.0	540.0	732.1	732.1	825.8	825.8	891.2	891.2	380.1	380.1	434.0	434.0	611.2	611.2
	298.3	503.0	503.0	503.0	421.0	421.0	620.3	620.3	666.8	666.8	872.1	872.1	294.2	294.2	339.1	339.1	486.8	486.8
Crystal long period (nm)	1.4	1.2	1.2	1.2	1.3	1.3	1.2	1.2	1.2	1.2	1.0	1.0	1.3	1.3	1.3	1.3	1.3	1.3
	8.5	9.1	9.1	9.1	8.8	8.8	8.2	8.2	11.6	11.6	12.1	12.1	8.6	8.6	8.8	8.8	9.5	9.5
	0.3	0.2	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2
Percentage of wind-back (%)																		
Oxygen transmission rate (cm ³ /m ² ·day·atm at23°C)	7	15	15	15	24	24	16	16	15	15	14	14	0	0	20	20	50	50
	59.1	55.3	55.3	55.3	49.7	49.7	38.2	38.2	19.6	19.6	5.6	5.6	42.7	42.7	44.2	44.2	79.0	79.0
	12.7	12.2	12.2	12.2	11.3	11.3	8.9	8.9	6.5	6.5	2.3	2.3	18.0	18.0	4.3	4.3	10.8	10.8
Water vapor transmission rate (g/m ² ·day at38°C, 90%RH)																		

[0113]

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12	
Draw ratio	3.7	5.0	5.0	2.0	1.0	4.3	5.3	6.3	8.0	3.5	5.0	5.0	
	4.3	6.0	5.0	2.0	8.6	1.0	1.0	1.0	1.0	10.0	7.0	10.0	
	0.9	0.8	1.0	1.0	0.1	4.3	5.3	6.3	8.0	0.4	0.7	0.5	
Drawing temperature (°C)	40	35	39	140	140	38	39	40	42	49	49	53	
	D	D	D	D	D	D	D	D	D	D	D	D	
	Incidence of tearing at time of rewinding												
Network structure	Absent	Absent	Absent	Present	Absent	Absent	Absent	Absent	Present	Present	Present	Present	
Fibril diameter (nm)	-	-	-	150.0	-	-	-	-	30.5	150.3	50.2	140.1	
	Average value			1.4	-	-	-	-	1.3	1.5	1.4	1.2	
	Standard deviation												
Tear strength (cN)	2.8	4.7	44.0	78.0	150.0	0.6	0.5	0.5	0.5	13.7	13.6	10.1	
	2.5	4.0	150.0	150.0	0.6	150.0	157.5	165.4	178.4	10.2	17.7	14.5	
	1.1	1.2	0.3	0.5	250.0	0.0	0.0	0.0	0.0	1.3	0.8	0.7	
Percentage of splitting problems (%)	31	28	42	42	42	42	42	42	46	44	42	44	
	32.0	35.0	2.7	2.0	0.0	10.0	20.0	25.0	35.1	15.9	22.3	22.3	
	26.6	31.0	1.0	1.0	32.0	3.0	7.0	10.0	6.4	7.0	10.0	10.7	
Thermal shrinkage (%) 120°C, 1 min	1.2	1.1	2.7	2.1	0.0	3.3	2.9	2.5	5.5	2.3	2.2	2.1	
	MD/ITD												
	Resistance to tearing after heating at 120°C												
Rigidity	D	D	D	D	D	D	D	D	D	D	D	D	
	D	D	D	D	D	A	A	A	D	A	B	A	
	10.3	10.0	10.0	10.0	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	
Thickness (μm)	1.2	2.6	0.8	0.5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	
	Adhesion workload (mJ/25cm²)												
	MD	97.0	96.0	21.0	66.0	50.0	450.0	472.5	496.1	78.4	453.2	203.6	427.7
Tensile strength (MPa)	99.0	94.0	12.0	37.0	450.0	50.0	45.0	40.5	77.2	373.4	176.1	353.3	
	TD												
	MD/ITD	1.0	0.8	1.8	1.8	0.1	9.0	10.5	12.3	1.0	1.2	1.2	1.2
Tensile elongation (%)	89.0	69.0	257.0	301.0	10.0	200.0	210.0	220.5	76.0	111.2	146.9	105.4	
	MD	102.0	102.0	177.0	453.0	200.0	10.0	9.0	8.1	110.2	146.7	136.3	
	TD												
Modulus (MPa)	MD/ITD	0.9	0.7	1.5	0.7	0.1	20.0	23.3	27.2	0.7	0.8	0.8	
	MD	370.0	347.0	237.0	274.0	250.0	950.0	997.5	1047.4	345.3	1027.1	573.0	980.8
	TD	270.0	232.0	223.0	255.0	950.0	250.0	225.0	202.5	845.0	451.5	804.9	
Crystal long period (nm)	1.4	1.5	1.1	1.1	0.3	3.8	4.4	5.2	1.4	1.2	1.3	1.2	
	MD/ITD												
	8.0	7.5	12.8	14.0	13.0	13.0	13.7	14.3	10.0	12.5	8.0	13.0	
Haze (%)	0.3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
	Percentage of wind-back (%)												
	77	80	80	80	80	81	82	84	84	82	83	82	
Percentage of oxygen transmission rate (cm³/m²·day·atm at23°C)	111.0	113.0	16169.1	2324.0	150.0	115.7	115.4	114.6	124.0	119.0	120.1	121.0	
	Oxygen transmission rate												
	23.1	21.9	30.9	116.0	25.0	21.7	22.3	21.1	25.2	22.4	21.5	24.1	
Water vapor transmission rate (g/m²·day at38°C, 90%RH)													

[0114]

Figure 2 shows the AFM phase image of the film surface obtained in Example 1. A homogeneous network structure was observed in Example 1. A network structure was also observed in Examples 2, 3, 4, 5, 6, 7, 8 and 9 and Comparative Examples 4, 9, 10, 11 and 12. Since the tensile strength, the tensile elongation and the tensile modulus fell within the specific ranges in Examples, the desired effects were obtained as shown in the evaluation results of Table 1. By contrast, since the tensile strength, the tensile elongation and the tensile modulus fell outside the specific ranges in Comparative Examples 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12, the desired effects were not obtained as shown in the evaluation results of Table 2. The AFM phase image of the film surface of Comparative Example 1 is shown in Figure 3.

Industrial Applicability

[0115]

The wrap film according to the present invention is a wrap film that has favorable adhesion in use, has rigidity, transparency, an anti-splitting effect and an anti-wind-back effect, is resistant to tearing even after heating at a high temperature (e.g., 120°C), has a low incidence of tearing at the time of rewinding, and is excellent in oxygen and water barrier properties, and as

such, can be suitably used as various wrap films for packaging including wrap films for food packaging.

Reference Signs List

[0116]

1: Extruder

2: Annular die

3: Die mouth

4: Tubular vinylidene chloride resin composition

(sock)

5: Sock liquid

6: Cool bath

7: First pinch roll

8: Parison

9: Second pinch roll

10: Bubble

11: Third pinch roll

12: Double-ply film

13: Wind-up roll

14: Pore

15: Fibril

Claims

[Claim 1]

A wrap film which has a tensile strength of 100 MPa or larger, a tensile elongation of 100% or less, and a tensile modulus of 280 MPa or larger in the transverse direction (TD),

which has a tensile modulus of 380 MPa or larger in the machine direction (MD),

which contains a polyvinylidene chloride resin composition,

and wherein draw ratio in the MD direction is larger than 3.4 and 4.0 or less, and draw ratio in the TD direction is 5.8 or more and 8.5 or less,

and wherein the wrap film has a network structure that is observed in an atomic force microscope phase image on a surface of at least one layer, wherein a network of the network structure is constituted by fibrils, and an average width of the fibrils observed in the network structure is 1 nm or larger and 145 nm or smaller.

[Claim 2]

The wrap film according to claim 1, wherein the wrap film has a crystal long period of 12.5 nm or smaller.

[Claim 3]

The wrap film according to claim 1 or 2, wherein as for a thermal shrinkage at 120°C measured in conformity

with ASTM D-2732, the thermal shrinkage in the machine direction (MD) is 4 to 30%, and a ratio of the thermal shrinkage in the machine direction (MD) to the thermal shrinkage in the transverse direction (TD) (MD/TD) is 2 or less.

[Claim 4]

The wrap film according to any one of claims 1 to 3, wherein the wrap film has an oxygen transmission rate equal to or lower than $110 \text{ cm}^3/\text{m}^2\cdot\text{day}\cdot\text{atm}$ at 23°C , and a water vapor transmission rate equal to or lower than $20 \text{ g}/\text{m}^2\cdot\text{day}$ at 38°C and 90% RH.

[Claim 5]

The wrap film according to any one of claims 1 to 4, wherein the wrap film has a thickness of 5 to $15 \text{ }\mu\text{m}$.

[Claim 6]

The wrap film according to any one of claims 1 to 5, wherein the wrap film comprises a copolymer containing 85 to 97% by mass of a vinylidene chloride monomer and 15 to 3% by mass of a vinyl chloride monomer.

[Claim 7]

A method for producing the wrap film according to any one of claims 1 to 6, comprising a step of drawing an undrawn sheet in the machine direction and the transverse direction, wherein a draw ratio in the machine direction is larger than 3.4 and 4.0 or less, and a draw ratio in the transverse direction is 5.8 or more and 8.5 or less.

[Claim 8]

A roll comprising the wrap film according to any one of claims 1 to 6 wound around a core.