

DESCRIPTION

TITLE

STRETCHED POLYPROPYLENE FILM

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FIELD

[0001]

The present invention relates to a stretched polypropylene film.

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BACKGROUND

[0002]

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Conventionally, stretched polypropylene films have been widely used for various purposes including packaging materials due to their excellent transparency, mechanical strength, moisture resistance, and stiffness. However, in recent years, from the perspective of reducing environmental impact, efforts have been made to reduce the amount of polypropylene used, such as reducing the thickness thereof, but users are demanding that the stiffness be maintained so as not to impair usability.

[0003]

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Specifically, it is necessary that thin stretched polypropylene films have significantly higher stiffness than conventional stretched polypropylene films. Since stretched polypropylene films are subjected to printing and lamination processes, it is necessary that they have sufficient heat resistance and dimensional stability while improving stiffness.

[0004]

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In order to solve these problems, there is known a technology in which a polypropylene having high stereoregularity and a narrow molecular weight distribution is used to form a stretched film, whereby a film having high-temperature stiffness and heat resistance is obtained (refer to Patent Literature 1). However, the polypropylene described in Patent Document 1 has a narrow stretchable temperature range, necessitating strict temperature control in the longitudinal and transverse stretching processes, and brings about the problem of an increase in the occurrence of defects due to the occurrence of stretching unevenness.

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[0005]

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Furthermore, there has been proposed a stretched film comprising a polypropylene composition containing two polypropylene components selected from polypropylenes having a pentad fraction, which is an indicator of high stereoregularity, of 92% or more, wherein the difference in pentad fraction values between the two is 1 to 5% (refer to Patent Literature 2). However, the stretched film is still not fully satisfactory since polypropylenes having a low pentad

fraction are used, though the stretchability is improved and the defect rate due to stretching unevenness is reduced as compared to the film described in Patent Literature 1. Further, the heat resistance and dimensional stability have not been investigated, and there is room for improvement.

[0006]

Further, there has been proposed a method which uses a propylene polymer composition composed of a propylene homopolymer and a propylene/ α -olefin random copolymer, wherein the composition has an α -olefin content of 0.3 to 1.6% by weight and an isotactic pentad index of 0.97 or more, the extraction amount by xylene is 3% or less, and the melt flow rate is 0.5 to 10 (g/10 min) (refer to Patent Literature 3). Regarding this method as well, the stretchability is not sufficient and stretching unevenness tends to occur.

[CITATION LIST]

[PATENT LITERATURE]

[0007]

[PTL 1] Japanese Unexamined Patent Publication (Kokai) No. 8-325327

[PTL 2] Japanese Unexamined Patent Publication (Kokai) No. 2009-235228

[PTL 3] Japanese Unexamined Patent Publication (Kokai) No. 2004-323542

SUMMARY

[TECHNICAL PROBLEM]

[0008]

In light of the points described above, the present invention aims to provide a stretched polypropylene film, wherein while the stiffness of the film is improved, suitable heat resistance and dimensional stability are provided to the film, stretchability of the film is suitable, it is possible to efficiently produce films of stable quality, and it is possible to contribute to increased production efficiency in secondary processing.

[SOLUTION TO PROBLEM]

[0009]

Specifically, a first invention relates to a stretched polypropylene film which is a laminated film comprising a base material layer and a surface layer laminated on one or both faces of the base material layer and having a dimensional change rate of 30% or less at 140 °C in an MD direction with a temperature rise from 30 °C to 150 °C at a rate of 5 °C/min and a load of 0.32 N applied thereto, as measured by a thermomechanical analyzer (TMA) and a TD direction storage modulus (E') of 600 MPa or more at 120 °C and a TD direction storage modulus (E') of 300 MPa or more at 140 °C, as measured in dynamic viscoelasticity measurement at a temperature rise rate

of 3 °C/min and a frequency of 1.0 Hz, wherein the base material layer is composed of a resin mixture of at least two different types containing a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more mixed with a propylene/ α -olefin random copolymer (B), and the propylene/ α -olefin random copolymer (B) is mixed at 1 to 10% by weight relative to 100% by weight of the resin mixture.

[0010]

A second invention relates to the stretched polypropylene film in the first invention, wherein the propylene/ α -olefin random copolymer (B) is at least one selected from a propylene/ethylene/1-butene random copolymer, a propylene/ethylene random copolymer, and a propylene/1-butene random copolymer.

[0011]

A third invention relates to the stretched polypropylene film in the second invention, wherein the propylene/ α -olefin random copolymer (B) is a propylene/ethylene/1-butene random copolymer.

[0012]

A fourth invention relates to the stretched polypropylene film in the third invention, wherein the propylene/ethylene/1-butene random copolymer has an ethylene content of 5 to 15 mol% and a butene content of 5 to 20 mol%.

[0013]

A fifth invention relates to the stretched polypropylene film in any one of the first to fourth inventions, wherein the laminated film has a heat shrinkage rate of 6.5% or less in each of the MD direction and TD direction in heat treatment at 150 °C for 5 minutes.

[0014]

A sixth invention relates to the stretched polypropylene film in any one of the first to fifth inventions, wherein a component amount of a crystal component (H) having a lowest mobility of three components used for approximation of a free induction decay curve at 70 °C in measurement using a pulsed NMR solid echo method is 55 to 70% and a component amount of an amorphous component (S) having a highest mobility thereof is 5 to 11% in the laminated film.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0015]

According to the stretched polypropylene film of the first invention, there is provided a stretched polypropylene film which is a laminated film comprising a base material layer and a surface layer laminated on one or both faces of the base material layer and having a dimensional change rate of 30% or less at 140 °C in an MD direction with a temperature rise from 30 °C to 150 °C at a rate of 5 °C/min and a load of 0.32 N applied thereto, as measured by a thermomechanical analyzer (TMA), and a TD direction storage modulus (E') of 600 MPa or more

at 120 °C and a TD direction storage modulus (E') of 300 MPa or more at 140 °C, as measured in dynamic viscoelasticity measurement at a temperature rise rate of 3 °C/min and a frequency of 1.0 Hz, wherein the base material layer is composed of a resin mixture of at least two different types containing a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more
5 mixed with a propylene/ α -olefin random copolymer (B), and the propylene/ α -olefin random copolymer (B) is mixed at 1 to 10% by weight relative to 100% by weight of the resin mixture, whereby while the stiffness of the film is improved, suitable heat resistance and dimensional stability are provided to the film, stretchability of the film is suitable, it is possible to efficiently produce films of stable quality, and it is possible to contribute to increased production efficiency
10 in secondary processing.

[0016]

According to the gas barrier resin composition of the second invention, in the first invention, the propylene/ α -olefin random copolymer (B) is at least one selected from a propylene/ethylene/1-butene random copolymer, a propylene/ethylene random copolymer, and a propylene/1-butene
15 random copolymer, whereby it is possible to improve stretchability while maintaining the dimensional stability and stiffness of the film.

[0017]

According to the stretched polypropylene film of the third invention, in the second invention, the propylene/ α -olefin random copolymer (B) is a propylene/ethylene/1-butene random copolymer,
20 whereby it is possible to improve stretchability while maintaining the dimensional stability and stiffness of the film.

[0018]

According to the stretched polypropylene film of the fourth invention, in the third invention, since the propylene/ethylene/1-butene random copolymer has an ethylene content of 5 to 15 mol% and a butene content of 5 to 20 mol%, whereby it is possible to improve stretchability while
25 maintaining the dimensional stability and stiffness of the film.

[0019]

According to the stretched polypropylene film of the fifth invention, in any one of the first to fourth inventions, the laminated film has a heat shrinkage rate of 6.5% or less in each of the MD
30 direction and TD direction in heat treatment at 150 °C for 5 minutes, whereby dimensional stability is excellent and it is possible to contribute to increased productivity.

[0020]

According to the stretched polypropylene film of the sixth invention, in any one of the first to fifth inventions, a component amount of a crystal component (H) having a lowest mobility of three
35 components used for approximation of a free induction decay curve at 70 °C in measurement using a pulsed NMR solid echo method is 55 to 70% and a component amount of an amorphous

component (S) having a highest mobility thereof is 5 to 11% in the laminated film, whereby it is possible to form a film having excellent stiffness and heat resistance while suppressing stretching unevenness.

DESCRIPTION OF EMBODIMENTS

[0021]

The stretched polypropylene film of the present invention is a film wherein a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more is used in the base material layer to provide the film with high stiffness and heat resistance, and a propylene/ α -olefin random copolymer (B) is mixed, whereby it is possible to improve stretchability and dimensional stability while maintaining stiffness of the film and increase productivity of films with stable quality and it is possible to contribute to improved production efficiency in secondary processing.

[0022]

The stretched polypropylene film of the present invention is a laminated film having a dimensional change rate of 30% or less at 140 °C in an MD direction with a temperature rise from 30 °C to 150 °C at a rate of 5 °C/min and a load of 0.32 N applied thereto, as measured by a thermomechanical analyzer (TMA), and a TD direction storage modulus (E') of 600 MPa or more at 120 °C and a TD direction storage modulus (E') of 300 MPa or more at 140 °C, as measured in dynamic viscoelasticity measurement at a temperature rise rate of 3 °C/min and a frequency of 1.0 Hz.

[0023]

A dimensional change rate at 140 °C in an MD direction with a temperature rise from 30 °C to 150 °C at a rate of 5 °C/min and a load of 0.32 N applied thereto, as measured by a thermomechanical analyzer (TMA), is an indicator for reproducing elongation of the film during heat drying when performing secondary processing of the film such as vapor deposition, printing, and lamination of metal or inorganic oxide layers, in a state in which the film is under tension, and as long as the film has a dimensional change rate of 30% or less, it is possible to contribute to production efficiency in secondary processing.

[0024]

Dynamic viscoelasticity measurement is a method of measuring the mechanical properties of a sample by applying strain or stress that changes over time (vibration) to the sample and measuring the resulting stress or strain. Temperature dependent and frequency dependent properties such as storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta (=E''/E')$) can be measured. Thus, various relaxation phenomena including glass transition can be observed, and information regarding the molecular structure and molecular motion of polymers can be obtained. Among the types of energy generated by external forces and strain on an object, storage modulus

(E') is the energy stored inside an object, and it can be said that the higher the storage modulus at high temperatures (120 °C to 140 °C), the better the elastic modulus, stiffness, and heat resistance in high-temperature environments. If the storage modulus is low, the elastic modulus decreases in high-temperature environments, resulting in inferior mechanical properties, leading to a decrease in stiffness and the film becoming more likely to elongate, which tends to induce wrinkles due to deformation. Specifically, films having a TD direction storage modulus (E') of 600 MPa or more at 120 °C and a TD direction storage modulus (E') of 300 MPa or more at 140 °C, as measured in dynamic viscoelasticity measurement at a temperature rise rate of 3 °C/min and a frequency of 1.0 Hz, exhibit excellent elastic modulus, stiffness, and heat resistance in high-temperature environments.

[0025]

Specifically, by setting the dimensional change rate in the MD direction in TMA measurement and the storage modulus in the TD direction in dynamic viscoelasticity measurement within the above ranges, a stretched polypropylene film having an excellent balance of stiffness, heat resistance, and dimensional stability can be obtained. In particular, such a film has excellent dimensional stability in high temperature environments, and when performing processing such as vapor deposition, printing, or lamination of metal or inorganic oxide layers on the stretched polypropylene film, elongation under high-temperature loads is reduced, wrinkles and deformation during the vapor deposition process, misregistration during printing, etc., are less likely to occur, processing efficiency is significantly improved, wrinkles and the like during lamination processing can be suppressed, and use in higher temperature environments is also enabled. Thus, it is possible to greatly contribute to increased production efficiency in secondary processing, such as films for food packaging and films for industrial use.

[0026]

It is necessary that the polypropylene resin (A) have a mesopentad fraction (mmmm) of 95% or more. When such a polypropylene resin (A) is used, crystallinity is easily improved, and a film having excellent stiffness and heat resistance can be obtained. When a polypropylene resin having a mesopentad fraction of less than 95% is used, the stiffness and heat resistance of the film tend to decrease. Further, the polypropylene resin (A) is not particularly limited as long as the mesopentad fraction (mmmm) thereof is 95% or more, and a polypropylene homopolymer or a copolymer containing ethylene or an α -olefin having 4 or more carbon atoms can be used. A propylene homopolymer which does not contain ethylene or an α -olefin having 4 or more carbon atoms is particularly preferable.

[0027]

The mesopentad fraction (mmmm) is an indicator of stereoregularity that can be obtained by high temperature nuclear magnetic resonance (NMR) measurement. The mesopentad fraction

(mmmm) can be measured using ^{13}C -NMR, and the mesopentad fraction can be calculated by the method described in “Zambelli et al., *Macromolecules*, Vol. 6, p. 925 (1973)”. The pentad fraction, which represents the degree of stereoregularity, indicates the proportion of isotactic chains in pentad units in the polypropylene molecular chain measured using ^{13}C -NMR, and is the fraction (mmmm) of propylene monomers at the center of a chain of five consecutive meso-bonded propylene units. Specifically, the intensity fraction of the mmmm peak among the total absorption peaks in the methyl carbon region of the ^{13}C -NMR spectrum is defined as an isotactic pentad unit.

[0028]

A propylene/ α -olefin random copolymer (B) is mixed with the polypropylene resin (A) described above to form a resin mixture, and a base material layer is formed therefrom. The propylene/ α -olefin random copolymer (B) is mixed at an amount of 1 to 10% by weight relative to 100% by weight of the resin mixture. These resins are mixed in accordance with the composition described above and used, whereby the stretchable temperature range is widened, and the defect rate due to stretching unevenness can be reduced, and it is possible to contribute to improved production efficiency. Furthermore, it becomes easier to adjust the dimensional change rate in the MD direction in TMA measurement and the storage modulus in the TD direction in dynamic viscoelasticity measurement to the values described above. Note that a masterbatch containing an antistatic agent, an anti-blocking agent, etc., may be mixed in the resin mixture, and other resins other than the above polypropylene resin (A) and propylene/ α -olefin random copolymer (B) may be mixed.

[0029]

The propylene/ α -olefin random copolymer (B) is a random copolymer of propylene and an α -olefin (excluding propylene), and examples of the α -olefin include ethylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, and 1-octene. These copolymers may be used alone or in combination of two or more thereto. Among propylene/ α -olefin random copolymers, propylene/ethylene random copolymers, propylene/ethylene/1-butene random copolymers, and propylene/1-butene random copolymers are preferable, and propylene/ethylene/1-butene random copolymers are more preferable.

[0030]

The propylene/ethylene/1-butene random copolymer preferably has an ethylene content of 1 to 15 mol% and a butene content of 1 to 20 mol%, further preferably an ethylene content of 5 to 15 mol% and a butene content of 5 to 20 mol%, and most preferably an ethylene content of 7 to 14 mol% and a butene content of 7 to 17 mol%. In the above ranges, the resin mixture primarily composed of a polypropylene resin having a high pentad fraction can be provided with suitable stretchability, and suitable stiffness and heat resistance can be maintained.

[0031]

The ethylene and butene contents of the propylene/ α -olefin random copolymer (B) are determined by a known method from the integrated intensity obtained by ^{13}C -NMR measurement. The ethylene content and butene content are determined by the following formulas (i-1) and (i-2).

$$\text{Ethylene content (mol\%)} = \text{IE} \times 100 / (\text{IE} + \text{IP} + \text{IB}) \quad \dots(\text{i-1})$$

$$\text{Butene content (mol\%)} = \text{IB} \times 100 / (\text{IE} + \text{IP} + \text{IB}) \quad \dots(\text{i-2})$$

[0032]

IE, IP, and IB are integrated intensities for ethylene, propylene, and butene, respectively, and are determined by the following formulas (i-3), (i-4), and (i-5).

$$\text{IE} = \text{I}_{\delta\delta} / 2 + \text{I}_{\gamma\delta} / 4 - \text{I}_{\beta\beta} + \text{I}_{\alpha\gamma}(\text{P}) + \text{I}_{\alpha\delta}(\text{P}) + \text{I}_{\alpha\gamma}(\text{B}) + \text{I}_{\alpha\delta}(\text{B}) \dots(\text{i-3})$$

$$\text{IP} = 1/3 \times [\text{I}_{\text{CH}_3}(\text{P}) + \text{I}_{\text{CH}}(\text{P}) + \text{I}_{\alpha\alpha}(\text{PP}) + 1/2 \times (\text{I}_{\alpha\alpha}(\text{PB}) + \text{I}_{\alpha\gamma}(\text{P}) + \text{I}_{\alpha\delta}(\text{P}))] \quad \dots(\text{i-4})$$

$$\text{IB} = 1/4 \times [\text{I}_{\text{CH}_3}(\text{B}) + \text{I}_{\text{CH}}(\text{B}) + \text{I}_{2\text{B}_2} + \text{I}_{\alpha\alpha}(\text{BB})) + 1/2 \times (\text{I}_{\alpha\alpha}(\text{PB}) + \text{I}_{\alpha\gamma}(\text{B}) + \text{I}_{\alpha\delta}(\text{B}))] \quad \dots(\text{i-5})$$

[0033]

The suffix (P) is a signal based on a methyl group branch derived from propylene, and likewise, (B) is a signal based on an ethyl group branch derived from butene. $\alpha\alpha(\text{PP})$ is a signal of methylene carbon based on a propylene chain, and likewise, $\alpha\alpha(\text{BB})$ is a signal of methylene carbon based on a butene chain, and $\alpha\alpha(\text{PB})$ is a signal of methylene carbon based on a propylene-butene chain.

[0034]

The following are substituted into formulas (i-3), (i-4), and (i-5) to determine the content of each component.

$$\text{I}_{\beta\beta} = \text{I}_{24.8-23.3}$$

$$\text{I}_{\gamma\delta} = \text{I}_{30.0-29.6}$$

$$\text{I}_{\delta\delta} = \text{I}_{29.6-29.2}$$

$$\text{I}_{\alpha\gamma}(\text{P}) + \text{I}_{\alpha\delta}(\text{P}) = \text{I}_{38.5-37.2}$$

$$\text{I}_{\alpha\gamma}(\text{B}) + \text{I}_{\alpha\delta}(\text{B}) = \text{I}_{34.5-33.5}$$

$$\text{I}_{\text{CH}_3}(\text{P}) = \text{I}_{22.6-18.0}$$

$$\text{I}_{\text{CH}}(\text{P}) = \text{I}_{29.2-27.9} + \text{I}_{31.1-30.0} + \text{I}_{33.5-32.2}$$

$$\text{I}_{\alpha\alpha}(\text{PP}) = \text{I}_{48.0-44.8}$$

$$\text{I}_{\text{CH}_3}(\text{B}) = \text{I}_{11.5-9.0}$$

$$\text{I}_{\text{CH}}(\text{B}) = \text{I}_{35.4-34.5} + \text{I}_{37.1-36.5} + \text{I}_{39.5-38.8}$$

$$\text{I}_{\alpha\alpha}(\text{BB}) = \text{I}_{40.2-39.5}$$

$$\text{I}_{\alpha\alpha}(\text{PB}) = \text{I}_{43.7-41.6}$$

$$\text{I}_{2\text{B}_2} = \text{I}_{26.9-26.0}$$

[0035]

The lower limit of the melting temperature (T_m) of the polypropylene resin (A) constituting the base material layer as measured by a differential scanning calorimeter (DSC) is preferably 162 °C, more preferably 163 °C, and further preferably 164 °C. When T_m is 162 °C or higher,

stiffness and heat resistance at high temperatures can be easily obtained. When the T_m of the propylene/ α -olefin random copolymer (B) is in the range of 120 to 165 °C, preferably 130 to 165 °C, and more preferably 140 to 165 °C, the balance of stiffness and heat resistance is excellent.

[0036]

5 The melt flow rate (MFR) (230 °C, 2.16 kgf) of the polypropylene resin (A) constituting the base material layer, from the viewpoint of extrusion moldability, is preferably 1 to 15 g/10 min, more preferably 1.5 to 10 g/10 min, and further preferably 2.0 to 8 g/10 min. The MFR (230 °C, 2.16 kgf) of the propylene/ α -olefin random copolymer (B) is preferably 5 to 15 g/10 min, and more preferably 6 to 10 g/10 min. Within the above ranges, the mechanical load tends to be small and
10 stretchability tends to be easy.

[0037]

The weight average molecular weight (M_w) of the polypropylene resin (A) constituting the base material layer as measured by gel permeation chromatography (GPC) is not particularly limited, and is preferably from 250,000 or more and 600,000 or less, and further preferably
15 300,000 or more and 550,000 or less. The molecular weight distribution (M_w/M_n) as expressed by the ratio (M_w/M_n) of weight average molecular weight (M_w) to number average molecular weight (M_n) is preferably 2 or more and 20 or less, and further preferably 4 or more and 10 or less. When they are within the above ranges, the resin has excellent fluidity, stretching during film forming is facilitated, and unevenness in thickness is reduced, contributing to improved
20 productivity. The GPC device used in the GPC method is not particularly limited, and a commercially available high-temperature GPC device which is capable of analyzing the molecular weight of polyolefins may be used.

[0038]

Furthermore, the laminated film of the present invention is a laminated film comprising a base
25 material layer and a surface layer laminated on one or both faces of the base material layer, and in the case of a base material layer and a surface layer laminated on one face thereof, the laminated film may have a one-type-two-layer structure, or may have a two-type-two-layer structure, and in the case of a base material layer and surface layers laminated on both faces thereof (first surface layer and second surface layer), the laminated film may have a one-type-three-layer structure, may
30 have a two-type-three-layer structure, or may have a three-type-three-layer structure.

[0039]

From the viewpoint of ensuring the stiffness, heat resistance, and dimensional stability of the laminated film, the pentad fraction of the polypropylene resin used for the surface layer is preferably 90% or more. However, when using a low-crystalline resin for the surface layer to
35 effectively bleed out antistatic properties or impart heat-sealing properties, it can be used within a range that does not impair the desired physical properties of the laminated film. Examples of low-

crystalline resins include random copolymers of propylene and α -olefins (excluding propylene), such as propylene/ethylene random copolymers, propylene/ethylene/1-butene random copolymers, and propylene/1-butene random copolymers. The thickness of the entire laminated film is preferably 9 to 100 μm , more preferably 10 to 80 μm , further preferably 12 to 60 μm , and particularly preferably 12 to 50 μm . The thickness of the surface layer can be adjusted within a range that does not impair the desired physical properties of the laminated film.

[0040]

As described above, additives may be appropriately added to the laminated film. Examples of additives include antioxidants, ultraviolet absorbers, antistatic agents, lubricants, nucleating agents, adhesives, antifogging agents, flame retardants, antiblocking agents, and inorganic or organic fillers. Examples of antistatic agents include aliphatic amine compounds such as lauryl diethanolamine, myristyl diethanolamine, and oleyl diethanolamine, aliphatic amide compounds such as lauryl diethanolamide, myristyl diethanolamide, and oleyl diethanolamide, and polyhydric alcohols. The antistatic agent can be added by a known method. For example, a high-concentration masterbatch may be prepared separately and mixed in any step, or may be mixed in advance with the polyolefin powder or polyolefin pellets. When preparing a high-concentration masterbatch, it can be obtained by, for example, heating and kneading a polyolefin resin and an antistatic agent using a known mixer or extruder such as a Banbury mixer, a Henschel mixer, a tumbler mixer, a single-screw extruder, or a multi-screw extruder.

[0041]

The heat shrinkage rate at 150 °C of the stretched polypropylene film of the present invention is preferably 6.5% or less in each of the MD and TD directions. As a result, a film having excellent mechanical properties, heat resistance, and dimensional stability in high-temperature environments can be obtained.

[0042]

In the stretched polypropylene film of the present invention, it is desirable that a component amount of a crystal component (H) having a lowest mobility of three components used for approximation of a free induction decay curve at 70 °C in measurement using a pulsed NMR solid echo method be 55 to 70% or less and a component amount of an amorphous component (S) having a highest mobility thereof be 5 to 11% or less. It is further preferable that the component amount of the crystal component (H) be 60% or more and 70% or less, and the component amount of the amorphous component (S) be 5 to 10% or less. As a result, a laminated film which has not only suitable stretchability but also a suitable balance of stiffness, heat resistance, and dimensional stability can be obtained.

[0043]

When the (H) component of the stretched polypropylene film is less than 55%, the stiffness

and heat resistance tend to be poor, and when 70% or more, the stretchability tends to deteriorate and the productivity tends to be poor. When the (S) component of the stretched polypropylene film is less than 5%, sufficient stretchability may not be obtained and stretching unevenness is likely to occur, and when it exceeds 11%, though the stretchability may be suitable, the stiffness and heat resistance tend to be inferior.

[0044]

Pulse NMR is an analytical method for evaluating the mobility of a polymer molecular chain as a whole system, and molecular mobility can be evaluated by measuring relaxation time and signal intensity at that time. Generally, the lower the mobility of the polymer chain, the shorter the relaxation time, and thus, the signal intensity decays faster, and the relative signal intensity, when the initial signal intensity is taken as 100%, decreases in a shorter time. Furthermore, the higher the mobility of the polymer chain, the longer the relaxation time, and thus, the signal intensity decays slower, and the relative signal intensity, when the initial signal intensity is taken as 100%, gradually decreases over a long period of time. A means for use of pulsed NMR and separation into three components for analysis is known.

[0045]

The free induction decay curve at 70 °C as measured by the pulsed NMR solid echo method is simultaneously fitted with a plurality of mixed components (H, M, S) in accordance with the following formula (ii), and the relaxation time T₂ of each component is calculated. The relaxation time T₂ is correlated with the mobility of molecules, and the shorter the relaxation time T₂, the lower the mobility of the molecules, and the longer the relaxation time T₂, the higher the mobility of the molecules. Furthermore, each component ratio is calculated in accordance with formulas (iii) to (v). The (M) component is a constrained amorphous component, has a relaxation time between the (H) component and the (S) component, and has molecular mobility between the (H) component and the (S) component.

$$A_{(t)} = A_{(0)H} \times \exp\{-(t/T_{2H})^{WH}\} + A_{(0)M} \times \exp\{-(t/T_{2M})^{WM}\} + A_{(0)S} \times \exp\{-(t/T_{2S})^{WS}\} \quad \dots(ii)$$

$$F_{(H)} = \{A_{(0)H} / (A_{(0)H} + A_{(0)M} + A_{(0)S})\} \times 100 \quad \dots(iii)$$

$$F_{(M)} = \{A_{(0)M} / (A_{(0)H} + A_{(0)M} + A_{(0)S})\} \times 100 \quad \dots(iv)$$

$$F_{(S)} = \{A_{(0)S} / (A_{(0)H} + A_{(0)M} + A_{(0)S})\} \times 100 \quad \dots(v)$$

t: Acquisition time

A_(t): Signal strength at acquisition time t

A_{(0)H}: Initial value of signal strength of (H) component (y-axis value at 0 on the x-axis)

A_{(0)M}: Initial value of signal strength of (M) component (y-axis value at 0 on the x-axis)

A_{(0)S}: Initial value of signal strength of (S) component (y-axis value at 0 on the x-axis)

T_{2H}: Relaxation time T₂ of (H) component

T_{2M}: Relaxation time T₂ of (M) component

T_{2S} : Relaxation time T_2 of (S) component
 W_H : Weibull coefficient of (H) component
 W_M : Weibull coefficient of (M) component
 W_S : Weibull coefficient of (S) component
5 F_H : Component ratio of (H) component
 F_M : Component ratio of (M) component
 F_S : Component ratio of (S) component

[0046]

10 The method for producing the stretched polypropylene film of the present invention is not particularly limited. An example is described below. The resins each constituting a layer are individually introduced into three extruders, then in such a manner to be laminated in the order of first surface layer/base material layer/second surface layer, coextruded from a three-layer T-die set at 200 to 250 °C, and cooled for solidification with cooling rollers at 20 °C to 60 °C to obtain a
15 raw sheet. It is preferable that the raw sheet be further introduced into a water tank. The cooling temperature is preferably 40 °C or lower. The cooling temperature is suitably 30 °C or lower so as not only to obtain transparency of the raw sheet but also to facilitate stretching in subsequent steps and reduce thickness unevenness.

[0047]

20 Next, the raw sheet is preheated to a set temperature of 110 °C to 140 °C, stretched 4 to 6-fold in the MD direction, and then annealed at 130 to 150 °C. Note that the stretching in the MD direction may be performed in two or more stages using three or more stretching rollers. When the stretching ratio in the MD direction is within the range described above, stretching in the TD direction stretching step is easy, whereby productivity is improved. Next, it is preheated in a tenter at a set temperature of 170 °C to 185 °C, and stretched 6 to 12-fold in the TD direction at a
25 stretching temperature of 155 °C to 170 °C. It is then annealed in an atmosphere of 160 to 175 °C at a 3 to 10% relaxation. Though the annealing temperature may be set high in order to reduce the thermal shrinkage rate, if it is set excessively high, the low molecular weight components will melt and recrystallize, which will roughen the film surface and lead to whitening. Though the heat shrinkage rate can be reduced by increasing the relaxation, if it is excessively increased, the
30 stiffness of the film tends to decrease. A roll sample of the stretched polypropylene film can be obtained by subjecting at least one face of the stretched polypropylene film obtained in this manner to a corona discharge treatment and then winding it with a winding machine.

EXAMPLES

35 **[0048]**

[Materials Used]

The inventors used the following materials to create stretched polypropylene films.

[0049]

<Polypropylene Resin (A)>

- Resin PP-1: manufactured by Japan Polypropylene Corporation, polypropylene resin “FL1105F”, mesopentad fraction (mmmm) = 96.1%, MFR = 3.5 g/10 min, T_m = 166 °C, M_w/M_n = 4.9
- Resin PP-2: manufactured by Prime Polymer Co., Ltd., polypropylene resin “F133A”, mesopentad fraction (mmmm) = 96.0%, MFR = 3.0 g/10 min, T_m = 166 °C, M_w/M_n = 4.8
- Resin PP-3: manufactured by Japan Polypropylene Corporation, polypropylene resin “FL100A”, mesopentad fraction (mmmm) = 91.0%, MFR = 3.0 g/10 min, T_m = 163 °C, M_w/M_n = 5.4

[0050]

<Propylene/α-Olefin Random Copolymer (B)>

- Resin PP-4: manufactured by Mitsui Chemicals, Inc., propylene/α-olefin random copolymer “PN2060”, MFR = 6.0 g/10 min, T_m = 162 °C, M_w/M_n = 2.2, ethylene content 11.4 mol %, butene content 7.1 mol%
- Resin PP-5: manufactured by Mitsui Chemicals, Inc., propylene/α-olefin random copolymer “PN3560”, MFR = 6.0 g/10 min, T_m = 162 °C, M_w/M_n = 2.2, ethylene content 10.5 mol %, butene content 16.1 mol%
- Resin PP-6: manufactured by Japan Polypropylene Corporation, propylene/α-olefin random copolymer “FW4BA”, MFR = 7.0 g/10 min, T_m = 138 °C, M_w/M_n = 5.2, ethylene content 2.8 mol%, butene content 2.8 mol%
- Resin PP-7: manufactured by Japan Polypropylene Corporation, propylene/α-olefin random copolymer “FX4EA”, MFR = 5.5 g/10 min, T_m = 131 °C, M_w/M_n = 5.0, ethylene content 1.3 mol%, butene content 5.1 mol%
- Resin PP-8: manufactured by Mitsui Chemicals, Inc., propylene/α-olefin random copolymer “XM-7070”, MFR = 7.0 g/10 min, T_m = 75 °C, M_w/M_n = 2.0, ethylene content 0 mol%, butene content 26.4 mol%

[0051]

<Additives>

An antistatic agent masterbatch (resin PP-9) was used as an additive. Resin PP-3 was used as a base, and the antistatic agent concentration was adjusted to 9%.

[0052]

[Measurement of Physical Properties of Materials Used]

<Mesopentad Fraction>

¹³C-NMR measurement was performed using an FT-NMR device (“JNM-ECA400” manufactured by JEOL RESONANCE Co., Ltd.). 0.6 mL of a mixed solution of deuterated orthodichlorobenzene: heavy benzene = 8:2 (volume ratio) was added to 120 mg of the sample,

heated to 135 °C to dissolve, and measured at 135 °C. The mesopentad fraction was calculated by the method described in “Zambelli et al., *Macromolecules*, Vol. 6, p. 925 (1973)”, and the assignment of peaks was performed based on the revised version of the above literature described in “*Macromolecules*, Vol. 8, p. 687 (1975).”

5 Observation nucleus: ^{13}C (100 MHz)

Measurement mode: single pulse proton broadband decoupling

Pulse interval: 5 seconds

Pulse width: 45°

Shift reference: solvent-derived signal = 132.39 ppm

10 Cumulated number: 11,000

[0053]

<Ethylene and Butene Content of Propylene/ α -olefin Random Copolymer (B)>

^{13}C -NMR measurement was performed using an FT-NMR device (“JNM-ECA400” manufactured by JEOL RESONANCE Co., Ltd.). 0.6 mL of a mixed solution of deuterated orthodichlorobenzene: heavy benzene = 8:2 (volume ratio) was added to 120 mg of the sample, heated to 135 °C to dissolve, and measured at 135 °C. The ethylene and butene contents were calculated by substituting the obtained integrated intensities into formulas (i-3), (i-4), and (i-5) as described above.

20 Observation nucleus: ^{13}C (100 MHz)

Measurement mode: single pulse proton broadband decoupling

Pulse interval: 5 seconds

Pulse width: 45°

Shift reference: solvent-derived signal = 132.39 ppm

Cumulated number: 11,000

25 **[0054]**

<Melting Temperature>

The melting temperature was determined by differential scanning calorimetry (DSC) measured in accordance with JIS K7121 (2012). Measurement was performed using a “DSC6200” manufactured by Seiko Instruments, Inc. (unit: °C)

30 **[0055]**

<Melt Flow Rate (MFR)>

The melt flow rate (MFR) was measured in accordance with method A of JIS K7210-1 (2014).

[0056]

<Molecular Weight, Molecular Weight Distribution Measurement>

35 The molecular weight and molecular weight distribution were measured using an “HLC-8321GPC-HT” manufactured by Tosoh Corporation under the following conditions:

Column: TSKgel GMHHR-H (20) HT × 3
(7.8 mm I.D. × 300 mm × 3)
Eluent: 1,2,4-trichlorobenzene (0.05% BHT added)
Flow rate: 1.0 mL/min
5 Detector: RI detector (Polarity: -)
Column temperature: 140 °C
Injection volume: 300 µL
Molecular weight standard: standard polystyrene

[0057]

[Preparation of Stretched Polypropylene Film]

<Production Example 1>

A composition including 95% by weight of resin PP-1 as the polypropylene resin (A) and 5% by weight of resin PP-4 as the propylene/α-olefin random copolymer (B) was dry-blended for the base material layer, and resin PP-3 was used as the resins of the first surface layer and the second surface layer. The three resins were individually introduced into three extruders, then in such a manner to be laminated in the order of first surface layer/base material layer/second surface layer, coextruded from a three-layer T-die set at 240 °C, brought into contact with a cooling roller at 30 °C, and then introduced into a 30 °C water bath as-is to obtain a raw sheet. Thereafter, the sheet was preheated at a set temperature of 135 °C, stretched five-fold in the MD direction, and then annealed at 140 °C. Next, the film was preheated in a tenter at a set temperature of 182 °C, stretched eight-fold in the TD direction at a stretching temperature of 163 °C, and then annealed at 170 °C while relaxing at 6.5%. Thereafter, one face was subjected to corona discharge treatment and then the film was wound using a winding machine to obtain the stretched polypropylene film of Production Example 1.

[0058]

<Production Example 2>

The stretched polypropylene film of Production Example 2 was obtained in the same manner as Production Example 1, except that a composition containing 87% by weight of resin PP-1 as the polypropylene resin (A), 3% by weight of resin PP-4 as the propylene/α-olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer.

[0059]

<Production Example 3>

The stretched polypropylene film of Production Example 3 was obtained in the same manner as Production Example 2, except that a composition containing 84% by weight of resin PP-1 as the polypropylene resin (A), 6% by weight of resin PP-4 as the propylene/α-olefin random

copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, the magnification in the TD direction was 8.7-fold, and the relaxation was 9.0%.

[0060]

<Production Example 4>

The stretched polypropylene film of Production Example 4 was obtained in the same manner as Production Example 2, except that a composition containing 87% by weight of resin PP-1 as the polypropylene resin (A), 3% by weight of resin PP-5 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, and the preheating temperature in the TD direction was 184 °C.

[0061]

<Production Example 5>

The stretched polypropylene film of Production Example 5 was obtained in the same manner as Production Example 2, except that a composition containing 84% by weight of resin PP-1 as the polypropylene resin (A), 6% by weight of resin PP-6 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, and the preheating temperature in the TD direction was 183 °C.

[0062]

<Production Example 6>

The stretched polypropylene film of Production Example 6 was obtained in the same manner as Production Example 3, except that a composition containing 81% by weight of resin PP-1 as the polypropylene resin (A), 9% by weight of resin PP-6 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, and the preheating temperature in the TD direction was 183 °C.

[0063]

<Production Example 7>

The stretched polypropylene film of Production Example 7 was obtained in the same manner as Production Example 2, except that a composition containing 84% by weight of resin PP-1 as the polypropylene resin (A), 6% by weight of resin PP-7 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer.

[0064]

<Production Example 8>

The stretched polypropylene film of Production Example 8 was obtained in the same manner as Production Example 2, except that a composition containing 84% by weight of resin PP-1 as the polypropylene resin (A), 6% by weight of resin PP-8 as the propylene/ α -olefin random

copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer.

[0065]

<Production Example 9>

The stretched polypropylene film of Production Example 9 was obtained in the same manner as Production Example 2, except that a composition containing 87% by weight of resin PP-2 as the polypropylene resin (A), 3% by weight of resin PP-4 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer.

[0066]

<Production Example 10>

The stretched polypropylene film of Production Example 10 was obtained in the same manner as Production Example 2, except that a composition containing 79% by weight of resin PP-1 as the polypropylene resin (A), 11% by weight of resin PP-4 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, the preheating temperature in the TD direction was 183 °C, the magnification in the TD direction was 8.7-fold, and the relaxation was 9.0%.

[0067]

<Production Example 11>

The stretched polypropylene film of Production Example 10 was obtained in the same manner as Production Example 10, except that a composition containing 78% by weight of resin PP-1 as the polypropylene resin (A), 12% by weight of resin PP-6 as the propylene/ α -olefin random copolymer (B), and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer.

[0068]

<Comparative Example 1-1>

The stretched polypropylene film of Comparative Example 1-1 was obtained in the same manner as Production Example 1, except that 100% by weight of resin PP-1 as the polypropylene resin (A) was used for the base material layer, the stretching temperature in the TD direction was 165 °C, and the annealing temperature in the TD direction was 168 °C.

[0069]

<Comparative Example 1-2>

The stretched polypropylene film of Comparative Example 1-2 was obtained in the same manner as Comparative Example 1-1, except that the preheating temperature in the TD direction was 185 °C and the stretching temperature in the TD direction was 163 °C.

[0070]

<Comparative Example 1-3>

The stretched polypropylene film of Comparative Example 1-3 was obtained in the same manner as Comparative Example 1-1, except that the preheating temperature in the TD direction was 180 °C and the stretching temperature in the TD direction was 165 °C.

[0071]

<Comparative Example 1-4>

The stretched polypropylene film of Comparative Example 1-4 was obtained in the same manner as Comparative Example 1-1, except that the preheating temperature in the TD direction was 178 °C and the stretching temperature in the TD direction was 168 °C.

[0072]

<Comparative Example 2>

The stretched polypropylene film of Comparative Example 2 was obtained in the same manner as Production Example 1, except that 100% by weight of resin PP-3 as the polypropylene resin (A) was used for the base material layer, the preheating temperature in the TD direction was 181 °C, the stretching temperature in the TD direction was 164 °C, and the annealing temperature in the TD direction was 168 °C.

[0073]

<Comparative Example 3>

The stretched polypropylene film of Comparative Example 3 was obtained in the same manner as Production Example 1, except that a composition containing 90% by weight of resin PP-3 as the polypropylene resin (A) and 10% by weight of resin PP-9 as the antistatic agent masterbatch was used for the base material layer, the preheating temperature in the TD direction was 181 °C, the stretching temperature in the TD direction was 164 °C, and the annealing temperature in the TD direction was 168 °C.

[0074]

The resin compositions and film forming conditions of the intermediate layer and surface layer of each Production Example and Comparative Example are summarized in Tables 1 to 3.

[0075]

[Table 1]

			Prod Ex 1	Prod Ex 2	Prod Ex 3	Prod Ex 4	Prod Ex 5	Prod Ex 6
Intermediate layer (wt%)	(A)	Resin PP-1	95	87	84	87	84	81
		Resin PP-2						
		Resin PP-3						
	(B)	Resin PP-4	5	3	6			
		Resin PP-5				3	6	9
		Resin PP-6						
		Resin PP-7						
		Resin PP-8						
	MB	Resin PP-9		10	10	10	10	10
Surface layer (wt%)		Resin PP-3	100	100	100	100	100	100
Film Production Conditions	Resin temp		(°C)	240	240	240	240	240
	Cooling roller temp		(°C)	30	30	30	30	30
	MD direction preheating temp		(°C)	135	135	135	135	135
	MD direction stretching rate		(fold)	5.0	5.0	5.0	5.0	5.0
	MD direction annealing temp		(°C)	140	140	140	140	140
	TD direction preheating temp		(°C)	182	182	182	184	183
	TD direction stretching temp		(°C)	163	163	163	163	163
	TD direction stretching rate		(fold)	8.0	8.0	8.7	8.0	8.7
	Relaxation		(%)	6.5	6.5	9.0	6.5	9.0
	TD direction annealing temp		(°C)	170	170	170	170	170

[0076]

[Table 2]

				Prod Ex 7	Prod Ex 8	Prod Ex 9	Prod Ex 10	Prod Ex 11	
Intermediate layer (wt%)	(A)	Resin PP-1		84	84		79	78	
		Resin PP-2				87			
		Resin PP-3							
	(B)	Resin PP-4				3	11		
		Resin PP-5							
		Resin PP-6						12	
		Resin PP-7		6					
		Resin PP-8			6				
	MB	Resin PP-9		10	10	10	10	10	
Surface layer (wt%)			Resin PP-3		100	100	100	100	100
Film Production Conditions	Resin temp		(°C)	240	240	240	240	240	
	Cooling roller temp		(°C)	30	30	30	30	30	
	MD direction preheating temp		(°C)	135	135	135	135	135	
	MD direction stretching rate		(fold)	5.0	5.0	5.0	5.0	5.0	
	MD direction annealing temp		(°C)	140	140	140	140	140	
	TD direction preheating temp		(°C)	182	182	182	183	183	
	TD direction stretching temp		(°C)	163	163	163	163	163	
	TD direction stretching rate		(fold)	8.7	8.7	8.7	8.7	8.0	
	Relaxation		(%)	9.0	9.0	9.0	9.0	6.5	
	TD direction annealing temp		(°C)	170	170	170	170	170	

[0077]

[Table 3]

			Comp Ex 1-1	Comp Ex 1-2	Comp Ex 1-3	Comp Ex 1-4	Comp Ex 2	Comp Ex 3
Intermediate layer (wt%)	(A)	Resin PP-1	100	100	100	100		
		Resin PP-2						
		Resin PP-3					100	90
	(B)	Resin PP-4						
		Resin PP-5						
		Resin PP-6						
		Resin PP-7						
		Resin PP-8						
	MB	Resin PP-9						10
Surface layer (wt%)		Resin PP-3	100	100	100	100	100	100
Film Production Conditions	Resin temp		(°C)	240	240	240	240	240
	Cooling roller temp		(°C)	30	30	30	30	30
	MD direction preheating temp		(°C)	135	135	135	135	135
	MD direction stretching rate		(fold)	5.0	5.0	5.0	5.0	5.0
	MD direction annealing temp		(°C)	140	140	140	140	140
	TD direction preheating temp		(°C)	182	185	180	178	181
	TD direction stretching temp		(°C)	165	163	165	168	164
	TD direction stretching rate		(fold)	8.0	8.0	8.7	8.0	8.0
	Relaxation		(%)	6.5	6.5	9.0	6.5	6.5
	TD direction annealing temp		(°C)	168	170	170	170	168

[0078]

[Performance Evaluation of Stretched Polypropylene Film]

For the evaluation of the stretched polypropylene film of each Production Example and Comparative Example, the dimensional change rate, storage modulus, heat shrinkage rate, pulse NMR, tensile modulus, and haze were measured. In addition, the thickness of each film was measured, and the appearance of the film was visually evaluated. The results are summarized in Tables 4 to 6. Note that Comparative Examples 1-2 to 1-4 were omitted from the tables because some of the various measurements could not be performed due to severe stretching unevenness during production. In Comparative Example 1-2, stretching unevenness occurred and whitening occurred, resulting in decreased transparency. In Comparative Example 1-3, stretching unevenness was even worse. In Comparative Example 1-4, the stretching unevenness was comparable to that of Comparative Example 1-3.

[0079]

<Dimensional Change Rate>

The dimensional change rate (%) was measured using a thermomechanical analyzer (“model number: Q400” manufactured by TA Instruments Japan Co., Ltd.) as a TMA measurement device. The stretched polypropylene film of each Production Example and Comparative Example was cut into a 8 mm × 4 mm test sample, and the test sample was affixed to the probe of the TMA device with the MD direction of the test sample as the tensile direction. A load of 0.32 N was applied to a test sample and the length (L_0) of the test sample at the time the load was initially applied was read. The test sample was then heated from 30 °C to 150 °C at a temperature rise rate of 5 °C/min, and the length (L_1) of the test sample after heating to 140 °C was read. During the series of heating, a load of 0.32 N was applied to the test sample in the MD direction of the test sample. The lengths (L_0) and (L_1) of the test sample before and after heating were then substituted into the following formula (vi), and the dimensional change rate (%) was calculated from the relationship between the initial test sample length and the amount of change. Note that since the stretched polypropylene film of Comparative Example 2 elongated to the measurement limit before the test sample reached 140 °C, and the dimensional change rate could not be calculated, it was determined as could not be measured, indicated as “-” in the tables. At this time, the dimensional change rate calculated from the elongation (L_1) at the measurement limit was 43.4%.

$$\text{Dimensional change rate (\%)} = \{(L_1 - L_0)/L_0\} \times 100 \quad \dots(\text{vi})$$

[0080]

<Storage Modulus>

The storage modulus (MPa) was measured in the TD direction at 120 °C and 140 °C using a “DVA-225” manufactured by IT Keisoku Seigyo Co., Ltd. under the following conditions.

Deformation mode: tension

Temperature range: -60 °C to 150 °C

Temperature rise rate: 3 °C/min

Frequency: 1 Hz

Environment: Air

[0081]

<Heat Shrinkage Rate>

The heat shrinkage rate (%) was measured in accordance with JIS Z 1712 (2009). A test sample of 15 mm in the TD direction and 200 mm in the MD direction was cut out from the stretched polypropylene film of each Production Example and Comparative Example, marked at a position 50 mm from both ends to determine the test length before heating (l_0), hung in a hot air oven at 150 °C, and heated for 5 minutes. Thereafter, it was removed, cooled at room temperature, and the length after heating was measured. The test length after heating was set as (l_1), and the heat shrinkage rate was determined by substituting it into the following formula (vii).

$$\text{Heat shrinkage rate (\%)} = \{(l_0 - l_1) / l_0\} \times 100 \dots (\text{vii})$$

[0082]

<Pulse NMR>

Pulse NMR (%) was measured using a pulse NMR device (“the minispec mq20” manufactured by Bruker Corp.) under the following conditions by cutting test samples of the stretched polypropylene film of each Production Example and Comparative Example with scissors and placing them in a sample tube. As the Weibull coefficient W_H , a value of 1.76 to 2.00 was used, and as the W_M and W_S , a value of 1 was used. The Weibull coefficient W_H was used as a variable in the fitting, and measurement was performed by changing each numerical value so as to accurately match the free induction decay curve.

Observation nucleus: ^1H (resonance frequency: 20 MHz)

Measurement temperature: 70 °C

Measurement method: Solid Echo method

90° pulse width: 3.26 μs

Pulse interval: 0.008 ms

Acquisition time: 2 ms

Repeat time: 1 sec

Cumulated number: 1024

[0083]

<Tensile Modulus>

Regarding the tensile modulus (GPa), the stretched polypropylene film of each Production Example and Comparative Example was cut into a test sample having a test direction length of 15 mm and width of 200 mm in each of the MD and TD directions to prepare cut-out test samples,

and the tensile elastic moduli in the MD direction and the TD direction were measured under the conditions of a distance between chucks of 100 mm and a tensile speed of 200 mm/min using a tensile tester (“RTF-1310” manufactured by A&D Company) in accordance with JIS K7127 (1999).

[0084]

<Haze>

Haze (%) was measured in accordance with JIS K 7136 (2000) using a haze meter (“NDH-5000” manufactured by Nippon Denshoku Industries Co., Ltd.).

[0085]

<Thickness>

Film thickness (μm) was measured using a thickness measuring device (“B-1” manufactured by Toyo Seiki Seisaku-sho, Ltd.) to determine the total layer thickness (μm).

[0086]

<Film Appearance Evaluation>

The film appearance was visually evaluated using the following criteria. Samples with substantially no stretching unevenness and a suitable appearance were evaluated as “Good”, and samples with stretching unevenness and a poor appearance were evaluated as “Poor”.

[0087]

[Table 4]

			Prod Ex 1	Prod Ex 2	Prod Ex 3	Prod Ex 4	Prod Ex 5	Prod Ex 6
Dimensional change rate		(%)	21.2	24.0	28.8	27.0	18.5	25.4
Storage modulus	120 °C	(MPa)	770	720	820	740	650	700
	140 °C		390	390	410	390	310	350
Heat shrinkage rate	MD direction	(%)	4.6	4.4	4.8	4.5	4.8	5.5
	TD direction		4.5	5.0	3.9	4.6	3.9	6.0
Pulse NMR	(H) component	(%)	66	69	55	68	68	60
	(M) component		27	25	34	25	27	33
	(S) component		7	6	11	7	5	7
	Weibull coefficient W _H		1.78	1.81	1.93	1.90	2.00	1.89
Tensile modulus	MD direction	(GPa)	2.3	2.3	2.2	2.2	2.4	2.4
	TD direction		4.9	4.8	4.6	4.7	4.8	4.9
Haze		(%)	1.2	1.3	1.3	1.5	1.5	1.3
Thickness		μm	19.3	19.7	20.1	20.0	20.2	20.0
Visual appearance evaluation			Good	Good	Good	Good	Good	Good

[0088]

[Table 5]

			Prod Ex 7	Prod Ex 8	Prod Ex 9	Prod Ex 10	Prod Ex 11
Dimensional change rate		(%)	21.2	29.5	19.1	-	32.0
Storage modulus	120 °C	(MPa)	740	730	890	680	710
	140 °C		360	390	460	350	350
Heat shrinkage rate	MD direction	(%)	5.1	5.0	4.3	5.7	6.2
	TD direction		6.2	4.7	5.3	3.3	6.7
Pulse NMR	(H) component	(%)	68	65	62	65	60
	(M) component		27	27	31	22	32
	(S) component		5	8	7	13	8
	Weibull coefficient W _H		1.76	1.80	1.93	1.94	1.83
Tensile modulus	MD direction	(GPa)	2.4	2.2	2.3	1.9	2.3
	TD direction		4.8	4.7	5.0	4.4	4.5
Haze		(%)	1.2	1.2	1.2	1.1	1.4
Thickness		μm	19.1	19.2	19.4	19.9	20.5
Visual appearance evaluation			Good	Good	Good	Good	Good

[0089]

[Table 6]

			Comp Ex 1-1	Comp Ex 2	Comp Ex 3
Dimensional change rate		(%)	16.4	33.6	37.9
Storage modulus	120 °C	(MPa)	880	460	510
	140 °C		440	210	220
Heat shrinkage rate	MD direction	(%)	4.2	6.2	7.4
	TD direction		5.7	7.1	8.5
Pulse NMR	(H) component	(%)	61	61	57
	(M) component		35	28	32
	(S) component		4	11	11
	Weibull coefficient W_H		2.00	2.00	2.00
Tensile modulus	MD direction	(GPa)	2.6	2.2	2.1
	TD direction		5.4	4.3	3.8
Haze		(%)	1.2	1.1	1.1
Thickness		μm	19.7	20.4	20.5
Visual appearance evaluation			Poor	Good	Good

[0090]

[Results and Discussion]

Production Examples 1 to 9 had small dimensional change rates in the MD direction at high temperatures and high storage moduli in the TD direction, and thus had excellent stiffness and heat resistance, as well as suitable dimensional stability. Furthermore, the films had no stretching unevenness in appearance and had excellent stretchability, resulting in suitable production efficiency.

[0091]

Though the film of Comparative Example 1-1, which was composed of only the polypropylene resin (A) having a high mesopentad fraction, had excellent stiffness, heat resistance, and dimensional stability, stretching unevenness occurred and the film was not of a quality level sufficient for use as a product. In the same manner as Comparative Example 1-1, in Comparative Examples 1-2 to 1-4 as well, in which only the polypropylene resin (A) having a high mesopentad fraction was used and the film forming conditions were changed, stretching unevenness could not be improved. From this, it could be understood that when the propylene/ α -olefin random copolymer (B) is mixed into the base material layer, the stretchability of the film can be improved and the occurrence of stretching unevenness can be suppressed.

[0092]

Though the films of Comparative Examples 2 and 3, in which polypropylene resins having a low mesopentad fraction were used, had excellent stretchability and stretching unevenness did not occur, the films were poor in stiffness, heat resistance, and dimensional stability, and thus, films having the desired physical properties could not be obtained.

[0093]

The films of Production Examples 10 and 11, in which the polypropylene resin (A) having a high mesopentad fraction was used and the amount of the propylene/ α -olefin random copolymer (B) was increased, were inferior in dimensional change rate and could not be used in high-temperature environments. Furthermore, in Production Example 11, in which the amount of the propylene/ α -olefin random copolymer (B) was increased as compared to Production Example 10, since the heat shrinkage rate was also inferior, it could be understood that when the amount of the propylene/ α -olefin random copolymer (B) is increased excessively, the stiffness, heat resistance, and dimensional stability tend to decrease, leading to a decrease in production efficiency.

[0094]

As shown above, in Production Examples 1 to 9, in which the base material layer was composed of a resin mixture in which the propylene/ α -olefin random copolymer (B) was mixed with the polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more, and in which the propylene/ α -olefin random copolymer (B) was mixed at 1 to 10% by weight with respect

to 100% by weight of the resin mixture, it was shown that it is possible to improve stretchability and reduce the defect rate due to stretching unevenness while maintaining good stiffness, heat resistance, and dimensional stability, contributing to increased efficiency in film production. Furthermore, since the dimensional stability under high temperature conditions is excellent, when performing processes such as vapor deposition, printing, and lamination of metal or inorganic oxide layers on the stretched polypropylene film, elongation due to load in high temperature conditions is less likely to occur, and wrinkles and deformation during the vapor deposition process, misregistration during printing, etc., can be suppressed, and wrinkling, etc., can be suppressed during lamination processing, whereby the stretched polypropylene film can be used even in higher temperature environments, significantly improving processing efficiency. Thus, it is possible to greatly contribute to increased production efficiency in secondary processing, such as films for food packaging and films for industrial use.

INDUSTRIAL APPLICABILITY

[0095]

To the stretched polypropylene film of the present invention, while the stiffness of the film is improved, suitable stretchability, heat resistance and dimensional stability are provided. In other words, according to the stretched polypropylene film of the present invention, it is possible to improve the productivity of films with stable quality while maintaining suitable stiffness, and since the stretched polypropylene film has suitable dimensional stability even under high temperature conditions, it is also possible to contribute to increased production efficiency in secondary processing.

CLAIMS

[Claim 1]

A stretched polypropylene film which is a laminated film comprising a base material layer
5 and a surface layer laminated on one or both faces of the base material layer and having

a dimensional change rate of 30% or less at 140 °C in an MD direction with a temperature rise
from 30 °C to 150 °C at a rate of 5 °C/min and a load of 0.32 N applied thereto, as measured by a
thermomechanical analyzer (TMA), and

a TD direction storage modulus (E') of 600 MPa or more at 120 °C and a TD direction storage
10 modulus (E') of 300 MPa or more at 140 °C, as measured in dynamic viscoelasticity measurement
at a temperature rise rate of 3 °C/min and a frequency of 1.0 Hz, wherein

the base material layer is composed of a resin mixture of at least two different types containing
a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more mixed with a
propylene/ α -olefin random copolymer (B), and

15 the propylene/ α -olefin random copolymer (B) is mixed at 1 to 10% by weight relative to 100%
by weight of the resin mixture.

[Claim 2]

The stretched polypropylene film according to claim 1, wherein the propylene/ α -olefin
20 random copolymer (B) is at least one selected from a propylene/ethylene/1-butene random
copolymer, a propylene/ethylene random copolymer, and a propylene/1-butene random copolymer.

[Claim 3]

The stretched polypropylene film according to claim 2, wherein the propylene/ α -olefin
25 random copolymer (B) is a propylene/ethylene/1-butene random copolymer.

[Claim 4]

The stretched polypropylene film according to claim 3, wherein the propylene/ethylene/1-
butene random copolymer has an ethylene content of 5 to 15 mol% and a butene content of 5 to
30 20 mol%.

[Claim 5]

The stretched polypropylene film according to any one of claims 1 to 4, wherein the laminated
film has a heat shrinkage rate of 6.5% or less in each of the MD direction and TD direction in heat
35 treatment at 150 °C for 5 minutes.

[Claim 6]

5 The stretched polypropylene film according to any one of claims 1 to 5, wherein a component amount of a crystal component (H) having a lowest mobility of three components used for approximation of a free induction decay curve at 70 °C in measurement using a pulsed NMR solid echo method is 55 to 70% and a component amount of an amorphous component (S) having a highest mobility thereof is 5 to 11% in the laminated film.