

Description

Title of Invention: BIAXIALY ORIENTED POLYPROPYLENE FILM
AND LAMINATE

Technical Field

[0001] The present invention relates to a biaxially oriented polypropylene film and a laminate using this film.

Background Art

[0002] Conventionally, oriented polypropylene films have been widely used for various applications, including packaging materials, due to their excellent transparency, mechanical strength, moistureproof property, stiffness, and other properties. In recent years, from the viewpoint of environmental burden reduction, efforts have been made to reduce the thickness and take other measures in order to decrease the amount of polypropylene used.

[0003] In thin oriented polypropylene films, users require the maintenance of stiffness in order not to impair usability, and therefore, it is necessary to significantly improve stiffness compared to conventional oriented polypropylene films. Moreover, since oriented polypropylene films are subjected to printing and lamination processes, sufficient heat resistance and dimensional stability are also required while improving

stiffness. Accordingly, biaxially oriented polypropylene films have been known, to which high heat resistance, stiffness, and other properties have been imparted by adjusting the heat shrinkage rate in the machine (MD) direction and transverse (TD) direction and impact strength (impact resistance) of the film (see, for example, Patent Literature 1).

[0004] Moreover, with the promotion of the sustainable development goals (SDGs), as an effort toward realizing an environmentally conscious, sound material-cycle society, measures such as using renewable energy in order to suppress the emission of greenhouse gases, including carbon dioxide, which is considered one of the causes of global warming, can be cited, for example. Therefore, in the field of resin films, films using plant-derived raw materials (biomass raw materials) instead of petroleum-derived raw materials have been proposed (see, for example, Patent Literature 2). Since plant-derived raw materials are carbon-neutral resources, they are effective as resources that can contribute to environmental burden reduction compared to petroleum-derived raw materials.

[0005] Furthermore, as an environmentally conscious effort, the use of recycled raw materials can be cited. As recycled raw materials expected to be used as materials constituting films, in addition to films to be reused, there are, for example, recycled materials

obtained by post-industrial recycling, in which materials generated in product manufacturing processes before being placed on the market, such as scraps including offcuts generated during film production and surplus products, are reused, and recycled materials obtained by post-consumer recycling, in which products used in the market are collected and recycled into resources. Moreover, as a method of molding these recycled raw materials, a method called mechanical recycling, in which the materials are crushed, melted, and pelletized at the time of reuse, is often used in general.

[0006] Among these mechanically recycled raw materials, those used in oriented polypropylene mainly use polypropylene as the main raw material. In such circumstances, materials different from the main raw material resin, such as resins of different types, as well as additives such as antistatic agents and antiblocking agents, and resins used in masterbatches of these additives, may be contained in unspecified proportions. These different materials contained in the recycled raw materials are technically or economically difficult to remove. Therefore, the recycled raw materials are reused with these different materials remaining.

[0007] In high-stiffness, high-heat-resistant biaxially oriented polypropylene films using such recycled raw materials, the presence of different materials contained

in the recycled raw materials tends to deteriorate film stiffness such as elastic modulus and film performance such as heat resistance. Therefore, conventionally, the use of these types of recycled raw materials in the production of high-stiffness, high-heat-resistant biaxially oriented polypropylene films has not been considered suitable and has not reached practical use. [0008] However, due to social requests for environmental consciousness, the use of recycled raw materials is required for the purpose of contributing to reducing greenhouse gas emissions, efficiently utilizing petroleum resources, and others. Moreover, the use of recycled raw materials is also economically rational and has become increasingly useful. Accordingly, the present inventors have conducted diligent studies and have succeeded in inventing a film that is excellent in film formability without impairing various types of film performance, even when using a recycled raw material containing different materials.

Citation List

Patent Literature

[0009] Patent Literature 1: Japanese Patent Laid-Open No. 2014-055283

Patent Literature 2: Japanese Patent Laid-Open No. 2021-133509

Summary of Invention

Technical Problem

[0010] The present invention has been made in view of the above points, and an object thereof is to provide a biaxially oriented polypropylene film and a laminate that are excellent in film formability without impairing stiffness or heat resistance, even when using a recycled raw material.

Solution to Problem

[0011] That is, a first invention relates to a biaxially oriented polypropylene film which is a laminated film comprising a base material layer and a surface layer laminated on one side or each of both sides of the base material layer, the base material layer containing a recycled raw material derived from a molded article mainly composed of a polypropylene resin, the laminated film having: an elastic modulus in a machine (MD) direction of 2.0 GPa or more and an elastic modulus in a transverse (TD) direction of 4.0 GPa or more, as measured in accordance with JIS K 7127 (1999); a difference between a dimensional change rate at 140°C in the machine (MD) direction, L_{140} (%), and a dimensional change rate at 120°C, L_{120} (%), $(L_{140} - L_{120})$, of 15 or less, as measured with a thermomechanical analyzer (TMA) with a temperature rise from 30°C to 150°C at 20°C/min under a load of 0.32 N applied in the machine (MD) direction; and a heat

shrinkage rate of 10% or less in each of the machine (MD) direction and the transverse (TD) direction in a heating treatment at 150°C for 5 minutes, wherein the base material layer is formed of a resin mixture in which at least two or more different resins are mixed, including: 55% by weight or more of a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more; and 5 to 25% by weight of the recycled raw material (B) having a melt flow rate (MFR) of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C, as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012), and a melting enthalpy (ΔH) of 87.0 J/g or more.

[0012] A second invention relates to the biaxially oriented polypropylene film according to the first invention, wherein the recycled raw material (B) has a crystallization temperature of 105°C or higher, as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012).

[0013] A third invention relates to the biaxially oriented polypropylene film according to the first or second invention, wherein a relationship of molecular weight distribution (M_w/M_n and M_{z+1}/M_w) of the recycled raw material (B), as determined by gel permeation chromatography (GPC) measurement, satisfies $M_w/M_n < M_{z+1}/M_w$ and $M_{z+1}/M_w \geq 4.7$.

[0014] A fourth invention relates to the biaxially oriented polypropylene film according to the first or second invention, wherein the base material layer contains 10% by weight or less of a propylene- α -olefin random copolymer (C).

[0015] A fifth invention relates to the biaxially oriented polypropylene film according to the third invention, wherein the base material layer contains 10% by weight or less of a propylene- α -olefin random copolymer (C).

[0016] A sixth invention relates to a laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to the first or second invention.

[0017] A seventh invention relates to a laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to the third invention.

[0018] An eighth invention relates to a laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to the fourth invention.

[0019] A ninth invention relates to a laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to the fifth invention.

[0020] A tenth invention relates to the laminate according to the sixth invention, wherein the sealant film is a cast polypropylene film.

[0021] An eleventh invention relates to the laminate according to the seventh invention, wherein the sealant film is a cast polypropylene film.

[0022] A twelfth invention relates to the laminate according to the eighth invention, wherein the sealant film is a cast polypropylene film.

[0023] A thirteenth invention relates to the laminate according to the ninth invention, wherein the sealant film is a cast polypropylene film.

Advantageous Effects of Invention

[0024] According to the biaxially oriented polypropylene film of the first invention, the film is a laminated film comprising a base material layer and a surface layer laminated on one side or each of both sides of the base material layer; the base material layer contains a recycled raw material derived from a molded article mainly composed of a polypropylene resin; the laminated film has an elastic modulus in a machine (MD) direction of 2.0 GPa or more and an elastic modulus in a transverse (TD) direction of 4.0 GPa or more as measured in accordance with JIS K 7127 (1999), a difference between a dimensional change rate at 140°C in the machine (MD) direction L_{140} (%) and a dimensional change rate at 120°C L_{120} (%) ($L_{140} - L_{120}$) of 15 or less as measured with a thermomechanical analyzer (TMA) with a temperature rise from 30°C to 150°C at 20°C/min under a load of 0.32 N

applied in the machine (MD) direction, and a heat shrinkage rate of 10% or less in each of the machine (MD) direction and the transverse (TD) direction in a heating treatment at 150°C for 5 minutes; and the base material layer is formed of a resin mixture in which at least two or more different resins are mixed, including 55% by weight or more of a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more, and 5 to 25% by weight of the recycled raw material (B) having a melt flow rate (MFR) of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012), and a melting enthalpy (ΔH) of 87.0 J/g or more, whereby excellent film formability can be obtained without impairing film performance such as stiffness or heat resistance, regardless of the presence or absence of different materials in the recycled raw material.

[0025] According to the biaxially oriented polypropylene film of the second invention, in the first invention, the recycled raw material (B) has a crystallization temperature of 105°C or higher as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012), whereby the crystallization rate becomes faster and good stiffness can be obtained.

[0026] According to the biaxially oriented polypropylene film of the third invention, in the first or second

invention, a relationship of molecular weight distribution (M_w/M_n and M_{z+1}/M_w) of the recycled raw material (B) as determined by gel permeation chromatography (GPC) measurement satisfies $M_w/M_n < M_{z+1}/M_w$ and $M_{z+1}/M_w \geq 4.7$, whereby high stiffness can be maintained.

[0027] According to the biaxially oriented polypropylene film of the fourth invention, in the first or second invention, the base material layer contains 10% by weight or less of a propylene- α -olefin random copolymer (C), the stretchable temperature range of the film can be broadened, thereby reducing the defect rate due to stretching unevenness and improving production efficiency.

[0028] According to the biaxially oriented polypropylene film of the fifth invention, in the third invention, the base material layer contains 10% by weight or less of a propylene- α -olefin random copolymer (C), whereby the stretchable temperature range of the film can be broadened, thereby reducing the defect rate due to stretching unevenness and improving production efficiency.

[0029] According to the laminate of the sixth invention, a sealant film is laminated on the biaxially oriented polypropylene film according to the first or second invention, whereby film performance such as stiffness or heat resistance is not impaired even when a recycled raw

material is compounded, and the laminate can be suitably used as a film product, such as a packaging film, that aims for environmental burden reduction.

[0030] According to the laminate of the seventh invention, a sealant film is laminated on the biaxially oriented polypropylene film according to the third invention, whereby film performance such as stiffness or heat resistance is not impaired even when a recycled raw material is compounded, and the laminate can be suitably used as a film product, such as a packaging film, that aims for environmental burden reduction.

[0031] According to the laminate of the eighth invention, a sealant film is laminated on the biaxially oriented polypropylene film according to the fourth invention, whereby film performance such as stiffness or heat resistance is not impaired even when a recycled raw material is compounded, and the laminate can be suitably used as a film product, such as a packaging film, that aims for environmental burden reduction.

[0032] According to the laminate of the ninth invention, a sealant film is laminated on the biaxially oriented polypropylene film according to the fifth invention, whereby film performance such as stiffness or heat resistance is not impaired even when a recycled raw material is compounded, and the laminate can be suitably used as a film product, such as a packaging film, that aims for environmental burden reduction.

[0033] According to the laminate of the tenth invention, in the sixth invention, the sealant film is a cast polypropylene film, whereby excellent recycling aptitude and heat sealing strength can be obtained.

[0034] According to the laminate of the eleventh invention, in the seventh invention, the sealant film is a cast polypropylene film, whereby excellent recycling aptitude and heat sealing strength can be obtained.

[0035] According to the laminate of the twelfth invention, in the eighth invention, the sealant film is a cast polypropylene film, whereby excellent recycling aptitude and heat sealing strength can be obtained.

[0036] According to the thirteenth invention, the laminate of the thirteenth invention, in the ninth invention, the sealant film is a cast polypropylene film, excellent recycling aptitude and heat sealing strength can be obtained.

Description of Embodiments

[0037] A biaxially oriented polypropylene film according to one embodiment of the present invention is a laminated film having a base material layer and a surface layer laminated on one side or each of both sides of the base material layer. This biaxially oriented polypropylene film contains a recycled raw material in the base material layer. The biaxially oriented polypropylene film of the present invention is produced by a known film

production method, such as the T-die method. This film is suitably used as, for example, a packaging film or the like for foods, daily necessities, miscellaneous goods, cosmetics, pharmaceuticals, and other products. The packaging film may also be formed into a bag as a packaging bag as appropriate.

[0038] The biaxially oriented polypropylene film satisfies the following as physical properties required for various applications such as packaging films: the elastic modulus in the machine (MD) direction is 2.0 GPa or more and the elastic modulus in the transverse (TD) direction is 4.0 GPa or more; the difference between the dimensional change rate in the machine (MD) direction, $(L_{140})\%$, and the dimensional change rate at 120°C, $(L_{120})\%$, $(L_{140} - L_{120})$, is 15 or less; and the heat shrinkage rate in each of the machine (MD) direction and the transverse (TD) direction is 10% or less.

[0039] The elastic modulus is a value measured by the test method for tensile characteristics in accordance with JIS K 7127 (1999). The elastic modulus is used as one of the indices of the stiffness of the film. A higher value of the elastic modulus indicates that the film has higher stiffness and a stronger stiff feeling. When the elastic modulus in the machine (MD) direction of the biaxially oriented polypropylene film is 2.0 GPa or more and the elastic modulus in the transverse (TD) direction is 4.0 GPa or more, excellent processing

aptitude to meet various applications such as packaging films can be obtained. When the elastic modulus in the machine (MD) direction or the elastic modulus in the transverse (TD) direction is too low, the film becomes one with inferior processing aptitude that is susceptible to deformation and the like, which may cause a reduction in productivity.

[0040] The dimensional change rate indicates the proportion at which the film is deformed due to a temperature rise, and is used as an index of dimensional stability such as elongation performance of the film. In particular, it relates to dimensional stability assuming a state where the film expands and contracts when tension is applied to the film during secondary processing of the film such as vapor deposition of a metal or inorganic oxide layer, printing, or lamination.

[0041] In the biaxially oriented polypropylene film of the present invention, the dimensional change rate at 140°C in the machine (MD) direction is defined as L_{140} (%) and the dimensional change rate at 120°C is defined as L_{120} (%), as measured with a thermomechanical analyzer (TMA) with a temperature rise from 30°C to 150°C at 20°C/min under a load of 0.32 N applied in the machine (MD) direction, and it is required that the difference between the dimensional change rate L_{140} and the dimensional change rate L_{120} , ($L_{140} - L_{120}$), is 15 or less. The difference between the dimensional change rates

(degree of dimensional stability) being 15 or less indicates that the proportion of deformation due to a temperature rise is small and the dimensional stability is excellent. When the difference between the dimensional change rates is too large, the film is susceptible to deformation due to a temperature rise and is inferior in dimensional stability. Therefore, the occurrence of wrinkles, deterioration of appearance, and other problems at the time of secondary processing such as printing may occur, leading to a reduction in productivity.

[0042] The heat shrinkage rate indicates the proportion at which the film shrinks at a predetermined temperature, and is used as an index of dimensional stability such as shrinkage performance of the film. In the biaxially oriented polypropylene film of the present invention, it is required that the heat shrinkage rate in each of the machine (MD) direction and the transverse (TD) direction in a heating treatment at 150°C for 5 minutes is 10% or less. When the heat shrinkage rate is 10% or less, it indicates that the film is less likely to shrink at a high temperature and is excellent in dimensional stability. When the heat shrinkage rate in either or both of the machine (MD) direction and the transverse (TD) direction is too large, the film is susceptible to shrinkage at a high temperature and is inferior in dimensional stability. Therefore, the occurrence of

wrinkles, deterioration of appearance, and other problems in the packaging process may occur, leading to a reduction in productivity.

[0043] Moreover, it is preferable that the biaxially oriented polypropylene film of the present invention has transparency required in applications such as packaging films. The transparency of the film is expressed by a haze value measured in accordance with JIS K 7136 (2000). A preferable haze value in the film is 5.0% or less. When the haze value is too large, transparency generally required in packaging films and the like is insufficient, which is not preferable.

[0044] The base material layer is formed of a resin mixture in which at least two or more different resins are mixed, including 55% by weight or more of a polypropylene resin (A) and 5 to 25% by weight of a recycled raw material (B). In addition to the above polypropylene resin (A) and recycled raw material (B), a propylene- α -olefin random copolymer (C), and additives such as a masterbatch containing an antistatic agent, an antiblocking agent, and the like are mixed into the base material layer as necessary.

[0045] It is required that the polypropylene resin (A) has a mesopentad fraction (mmmm) of 95% or more. The mesopentad fraction (mmmm) is an index of stereoregularity that can be obtained by high temperature nuclear magnetic resonance (NMR) measurement. As for the

measurement of the mesopentad fraction (mmmm), ^{13}C -NMR measurement was performed using a FT-NMR apparatus ("JNM-ECA400" manufactured by JEOL RESONANCE Co., Ltd.). 0.6 mL of a mixed solution of deuterated ortho-dichlorobenzene and deuterated benzene in a volume ratio of 8:2 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)".

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

Cumulative number: 11,000

[0046] 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. This pentad fraction 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 isotactic pentad units.

[0047] By making the base material layer mainly contain a polypropylene resin having a mesopentad fraction (mmmm) of 95% or more, crystallinity is likely to be improved, and the resin layer exhibits excellent stiffness and heat resistance. When the compounding proportion of this polypropylene resin is too small, the stiffness, heat resistance, and other properties of the film may be deteriorated. Similarly, when the mesopentad fraction of the polypropylene film is less than 95%, the stiffness, heat resistance, and other properties of the film may also be deteriorated.

[0048] The recycled raw material (B) is a resin material mainly derived from polypropylene resin molded articles such as film molded articles, scraps including offcuts generated during film production, surplus products, and other resin products, which is obtained by subjecting them to reprocessing into raw material such as re-pelletizing. This recycled raw material also includes resin molded articles in which different materials remain, such as resins of different types from the resin used as the main raw material, additives such as antistatic agents and antiblocking agents, and resins used in masterbatches of these additives, which are difficult-to-remove materials different from the main raw

material. When a recycled raw material containing such different materials remaining in resin molded articles is used as a constituent material of a biaxially oriented polypropylene film, it usually causes deterioration of film stiffness such as elastic modulus and film performance such as heat resistance. In addition, in the biaxially oriented polypropylene film of the present invention, since the main raw material of the base material layer is a highly crystalline polypropylene resin, cases where the recycled raw material contains a resin having low crystallinity may also cause deterioration of film performance.

[0049] Accordingly, in the biaxially oriented polypropylene film of the present invention, it has been found that, by focusing on the melt flow rate, melting peak temperature, and melting enthalpy of the recycled raw material to be compounded, and by using a recycled raw material having a melt flow rate, melting peak temperature, and melting enthalpy under predetermined conditions, excellent film formability can be obtained without impairing film performance such as stiffness or heat resistance, regardless of the presence or absence of different materials that cause deterioration of film performance.

[0050] That is, the recycled raw material is required to have a melt flow rate (MFR) of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C, and a melting

enthalpy (ΔH) of 87.0 J/g or more. The preferable conditions for the melt flow rate (MFR), melting peak temperature, and melting enthalpy (ΔH) of the recycled raw material are all set taking the presence of different materials into consideration.

[0051] The melt flow rate (MFR) is used as an index of the fluidity of the resin. A larger value of MFR indicates better fluidity. When a recycled raw material with too small a MFR is used, it may cause deterioration of film moldability due to insufficient fluidity. When the MFR is too large, it may cause deterioration of film moldability due to excessive fluidity. By using a recycled raw material with a MFR of 3.0 to 11.0 g/10 min, good film moldability can be obtained even in the case where the recycled raw material contains different materials.

[0052] The melting peak temperature is a value measured by a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012). The melting peak temperature is used as one of the indices of the heat resistance of the resin. When a recycled raw material with too low a melting peak temperature is used, insufficient heat resistance may cause a large heat shrinkage rate of the film, making the film susceptible to thermal deformation, and the stiffness and dimensional stability of the film may also be deteriorated. Also, regarding the melting peak temperature, since almost no

examples are observed in which the melting peak temperature of resin molded articles usable as recycled raw materials exceeds 170°C, 170°C is considered appropriate as a practical upper limit value. Therefore, by using a recycled raw material with a melting peak temperature of 145 to 170°C, good heat resistance can be obtained even in the case where the recycled raw material contains different materials, suppressing thermal deformation of the film, and deterioration of the stiffness and dimensional stability of the film can also be suppressed.

[0053] The melting enthalpy (ΔH) is the energy required for the resin to melt, measured by a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012). The melting enthalpy is used as one of the indices of the heat resistance of the resin. When a recycled raw material with too low a melting enthalpy is used, insufficient heat resistance may cause the film to be susceptible to thermal deformation, and the stiffness and dimensional stability of the film may also be deteriorated. The melting enthalpy of the recycled raw material is required to be 87.0 J/g or more from the viewpoint of thermal stability, which allows good heat resistance to be obtained even in the case where the recycled raw material contains different materials, suppressing thermal deformation of the film, and

deterioration of the stiffness and dimensional stability of the film can also be suppressed.

[0054] Moreover, it is preferable that the recycled raw material has a crystallization temperature of 105°C or higher. The crystallization temperature is a value measured by a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012). The crystallization temperature affects the stiffness, heat resistance, moldability, and other properties of the biaxially oriented polypropylene film. When the crystallization temperature of the recycled raw material is too low, insufficient heat resistance may cause the film to be susceptible to thermal deformation, and the stiffness, dimensional stability and other properties of the film may also be deteriorated. When the crystallization temperature of the recycled raw material is 105°C or higher, the crystallization rate becomes faster and good stiffness can be obtained, and deterioration of the dimensional stability of the film and other problems can be suppressed.

[0055] Furthermore, it is preferable that the relationship of molecular weight distribution (M_w/M_n and M_{z+1}/M_w) of the recycled raw material, as determined by gel permeation chromatography (GPC) measurement, satisfies $M_w/M_n < M_{z+1}/M_w$ and $M_{z+1}/M_w \geq 4.7$. In the above molecular weight distribution, M_w is the weight average molecular weight, which is a value obtained by

multiplying the number of each molecule by its molecular weight and then determining their average. M_n is the number average molecular weight, which is a value obtained by simply averaging the configuration of molecules by number.

[0056] M_{z+1} ($Z+1$ -average molecular weight) is more susceptible to the influence of the high molecular weight fraction than M_z , which is a value already susceptible to the presence of high molecular weight than M_w . Note that M_{z+1} and M_z (Z -average molecular weight) are defined by the following expression (i) and the following expression (ii), respectively.

$$M_{z+1} = \Sigma (N_i \cdot M_i^4) / \Sigma (N_i \cdot M_i^3) \dots (i)$$

$$M_z = \Sigma (N_i \cdot M_i^3) / \Sigma (N_i \cdot M_i^2) \dots (ii)$$

[0057] M_w/M_n is an index representing the molecular weight distribution of each molecule. Meanwhile, M_{z+1}/M_w is an index representing the molecular weight distribution of the high molecular weight component. In the relationship of the molecular weight distribution, in the case of $M_w/M_n < M_{z+1}/M_w$, it indicates that the molecular weight distribution of the high molecular weight component is broad, very high molecular weight components are present, and their proportion is high. By using a recycled raw material having such a high molecular weight component in a large amount, high stiffness can be maintained in the biaxially oriented polypropylene film. Moreover, M_{z+1}/M_w in that case is

4.7 or more. When M_z+1/M_w is too low, the proportion of the high molecular weight component is insufficient, which may make it impossible to maintain high stiffness.

[0058] The propylene- α -olefin random copolymer (C) is a resin material compounded as necessary in order to broaden the stretchable temperature range of the film, thereby reducing the defect rate due to stretching unevenness and improving production efficiency. By compounding the propylene- α -olefin random copolymer in the base material layer of the film, it becomes easier to adjust properties such as the dimensional change rate in the MD direction in TMA measurement. In the case where the propylene- α -olefin random copolymer is compounded, its proportion is preferably 10% by weight or less. When the propylene- α -olefin random copolymer is contained in too large an amount, the stiffness, heat resistance, and other properties of the film may be deteriorated.

[0059] The propylene- α -olefin random copolymer to be compounded in the base material layer is a random copolymer of propylene and an appropriate α -olefin other than propylene. 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 singly or in combinations of two or more thereof. Among the propylene- α -olefin random copolymers, a propylene-ethylene random copolymer, a propylene-ethylene-1-butene random copolymer, and a propylene-1-butene random

copolymer are preferable, and a propylene-ethylene-1-butene random copolymer is still more preferable.

[0060] The surface layer is a resin layer laminated on one side or each of both sides of the base material layer. The surface layer is a layer subjected to secondary processing of the film, such as vapor deposition, printing, or lamination. From the viewpoint of recycling aptitude, it is preferable that the resin material constituting the surface layer is mainly composed of a polypropylene resin that is the same type of resin material as that of the base material layer. As the polypropylene resin, the same type of polypropylene resin as that of the base material layer may be used, or a different type of polypropylene resin may be used. For example, in the case where the surface layer is laminated on one surface of the base material layer, the film can have a one-type two-layer structure or a two-type two-layer structure. Also, in the case where the surface layer is laminated on each of both surfaces of the base material layer, the film can have a one-type three-layer structure, a two-type three-layer structure, or a three-type three-layer structure. Furthermore, as a biaxially oriented film of three or more layers, any optional layer such as an intermediate layer may be laminated between the base material layer and the surface layer as necessary.

[0061] In the surface layer, the pentad fraction of the polypropylene resin to be used is preferably 90% or more from the viewpoint of ensuring the stiffness, heat resistance, dimensional stability, and other properties of the film. Moreover, in the case where antistatic performance is to be effectively bled out or heat sealing performance is to be imparted, it is also possible to use a resin of low crystallinity to the extent that the desired physical properties of the laminated film are not impaired. Examples of the resin of low crystallinity include random copolymers of propylene and an α -olefin (excluding propylene), such as a propylene-ethylene random copolymer, a propylene-ethylene-1-butene random copolymer, and a propylene-1-butene random copolymer.

[0062] In the biaxially oriented polypropylene film, additives are added as appropriate, as necessary. Examples of the additives include an antioxidant, an ultraviolet absorber, an antistatic agent, a lubricant, a nucleating agent, an adhesive, an antifogging agent, a flame retardant, an antiblocking agent, and an inorganic or organic filler. As the antistatic agent, for example, there may be mentioned 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 separately fabricated and mixed in an arbitrary step, or it may be mixed in advance with a polyolefin powder or polyolefin pellets. When fabricating the high-concentration masterbatch, for example, it can be obtained by 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.

[0063] The thickness of the biaxially oriented polypropylene film is set as appropriate depending on the application or the like. For example, 9 to 100 μm is preferable, 10 to 80 μm is more preferable, 12 to 60 μm is still more preferable, and 12 to 50 μm is particularly preferable. In the biaxially oriented polypropylene film, the thickness of the surface layer is also adjusted as appropriate to the extent that the desired physical properties of the film are not impaired. For example, 0.1 to 10 μm is preferable, and 0.5 to 8 μm is more preferable.

[0064] The biaxially oriented polypropylene film of the present invention, as described above, is a laminated film in which the recycled raw material (B) is compounded in the base material layer to aim for environmental burden reduction. In particular, it is characterized by using as the recycled raw material to be compounded a recycled raw material that satisfies all of the

conditions of a melt flow rate (MFR) of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C, and a melting enthalpy (ΔH) of 87.0 J/g or more, and by setting the compounding proportion thereof to 5 to 25% by weight. Conventionally, when a recycled raw material is used as a film constituent material, the film performance such as stiffness or heat resistance may be deteriorated due to the influence of different materials in the recycled raw material. However, by compounding an appropriate amount of the recycled raw material satisfying all of the above conditions in the base material layer, excellent film formability can be obtained without impairing film performance such as stiffness or heat resistance, regardless of the presence or absence of different materials in the recycled raw material. Therefore, in the field of resin films where the use of recycled raw materials has been difficult, the reuse of recycled raw materials can be promoted, thereby greatly contributing to environmental burden reduction.

[0065] In the biaxially oriented polypropylene film of the present invention, a sealant film can be laminated on the surface layer or on the side of the base material layer where no surface layer has been provided, thereby forming a laminate. As the sealant film, a single-layer or multi-layer resin film having heat sealability is suitably used.

[0066] In the sealant film, an appropriate resin material having heat sealing performance can be used; however, from the viewpoint of recycling aptitude, it is preferable that the sealant film is mainly composed of a polypropylene resin that is the same type of resin material as that of the base material layer or the surface layer. The polypropylene resin can be selected from general polypropylene-based resins. For example, it is selected from at least one or more of the following: a propylene homopolymer, a propylene- α -olefin random copolymer such as a propylene-ethylene random copolymer or a propylene-ethylene-butene random copolymer, and a propylene-ethylene block copolymer.

[0067] It is also preferable that the sealant film is a cast polypropylene film using the above-described polypropylene resin. A cast film is suitable as the sealant film because, due to its low film orientation, it exhibits high heat sealing strength. Note that the term "cast" means a state in which no intentional stretching has been performed, and it also includes cases where unavoidable stretching has been applied during film formation or the like.

[0068] The laminate obtained in this way includes a biaxially oriented polypropylene film containing a recycled raw material and a sealant layer, and it can thus be suitably used as a film product, such as a

packaging film, that aims for environmental burden reduction.

Examples

[0069] [Fabrication of Biaxially Oriented Polypropylene Film]

When fabricating the biaxially oriented polypropylene films of Trial Production Examples 1 to 24, the respective materials described later were kneaded and melted based on predetermined compounding proportions (% by weight), and co-extruded by the T-die method to form a three-layer structure composed of a base material layer, and a first surface layer and a second surface layer laminated on each of both surfaces thereof, thereby obtaining a raw sheet-shaped product. Next, the raw sheet-shaped product was oriented by 5.0 times in the machine (MD) direction and then oriented by 8.0 times in the transverse (TD) direction, thereby obtaining a biaxially oriented polypropylene film composed of a first surface layer, a base material layer, and a second surface layer. The compounding proportions and other details of the resin materials used in each layer of Trial Production Examples 1 to 24 are shown in Tables 1 to 4 below.

[0070] [Materials Used]

The following resins were used as resin materials for the respective layers. The melt flow rate (MFR) of

each material was the value measured using a melt indexer (G-01, manufactured by Toyo Seiki Seisaku-sho, Ltd.) in accordance with JIS K 7210 (2014) at a test temperature of 230°C. Also, the crystallization temperature (°C), melting peak temperature (°C), and melting enthalpy (J/g) of the recycled raw material were each measured using a differential scanning calorimeter (DSC214 Polyma, manufactured by NETZSCH). In this measurement, a measurement (1st Run) was carried out, which involved heating from 20°C to 200°C at a rate of 10°C/min under a stream of nitrogen, holding at 200°C for 3 minutes, and then cooling from 200°C to 20°C at a rate of 10°C/min. Thereafter, a measurement (2nd Run) was carried out, which involved holding at 20°C for 3 minutes and then heating from 20°C to 200°C at a rate of 10°C/min. From the obtained DSC curve of the 1st Run, the exothermic peak temperature was determined as the crystallization temperature (°C), while the melting peak temperature and the melting enthalpy were determined from the DSC curve of the 2nd Run. Note that, in the case where multiple melting peaks were present, the highest melting peak temperature was used, and the melting enthalpy was determined by setting a baseline connecting 50°C to 180°C on the DSC curve with a linear line.

[0071] Also, the molecular weight and molecular weight distribution of each material were measured using a high-temperature type GPC apparatus ("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

Detector: RI detector (Polarity: -)

Column temperature: 140°C

Injection volume: 300 µL

Molecular weight standard: standard polystyrene

[0072] <Polypropylene Resin (A)>

- Resin A1: propylene homopolymer (mesopentad fraction (mmmm) 96.1%, MFR 3.5 g/10 min, melting peak temperature 166°C)

- Resin A2: propylene homopolymer (mesopentad fraction (mmmm) 95.8%, MFR 4.6 g/10 min, melting peak temperature 166°C)

- Resin A3: propylene homopolymer (mesopentad fraction (mmmm) 91.0%, MFR 3.0 g/10 min, melting peak temperature 163°C)

[0073] <Recycled Raw Material (B)>

- Resin B1: recycled raw material composed of biaxially oriented polypropylene film (commercial product, resin composition: 99.4% by weight of polypropylene resin and 0.6% by weight of polyethylene resin) (MFR 5.4 g/10 min, melting peak temperature 162°C,

melting enthalpy 100.2 J/g, crystallization temperature 112°C, Mw/Mn: 4.3, and Mz+1/Mw 5.0)

- Resin B2: recycled raw material composed of biaxially oriented polypropylene film (commercial product, resin composition: 97.0% by weight of polypropylene resin and 3.0% by weight of polyethylene resin) (MFR 5.7 g/10 min, melting peak temperature 161°C, melting enthalpy 100.5 J/g, crystallization temperature 114°C, Mw/Mn 4.3, and Mz+1/Mw 4.8)

- Resin B3: recycled raw material composed of cast polypropylene film (commercial product, resin composition: 98.5% by weight of polypropylene resin and 1.5% by weight of polyethylene resin) (MFR 10.1 g/10 min, melting peak temperature 150°C, melting enthalpy 87.6 J/g, crystallization temperature 117°C, Mw/Mn 4.6, and Mz+1/Mw 4.9)

- Resin B4: recycled raw material composed of polypropylene bottle (commercial product, resin composition: mainly composed of polypropylene resin (details unknown)) (MFR 10.1 g/10 min, melting peak temperature 140°C, melting enthalpy 86.8 J/g, crystallization temperature 102°C, Mw/Mn 4.8, and Mz+1/Mw 4.6)

[0074] <Propylene- α -Olefin Random Copolymer (C)>

- Resin C1: propylene- α -olefin random copolymer (MFR 6.0 g/10 min, melting peak temperature 162°C)

[0075] <Additive>

An antistatic agent masterbatch (resin D1: MFR 7.8 g/10 min) was used as an additive. Resin A3 was used as a base, and adjustment was made so that the concentration of the antistatic agent was 9%.

[0076] [Trial Production Example 1]

Trial Production Example 1 is a film obtained by compounding 100% by weight of resin A3, which is a polypropylene resin, used as the first surface layer, 80% by weight of resin A1, which is a polypropylene resin, 10% by weight of resin B1, which is a recycled raw material, and 10% by weight of resin D1, which is an additive (antistatic agent masterbatch), used as the base material layer, and 100% by weight of resin A3, which is a polypropylene resin, used as the second surface layer to forming a film with a thickness of 20 μm .

[0077] [Trial Production Example 2]

Trial Production Example 2 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the amount of resin A1 was set to 75% by weight and the amount of resin B1 was set to 15% by weight in the base material layer.

[0078] [Trial Production Example 3]

Trial Production Example 3 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the amount of resin A1 was set to 70% by weight and the amount of resin B1 was set to 20% by weight in the base material layer.

[0079] [Trial Production Example 4]

Trial Production Example 4 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the amount of resin A1 was set to 65% by weight and the amount of resin B1 was set to 25% by weight in the base material layer.

[0080] [Trial Production Example 5]

Trial Production Example 5 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the recycled raw material in the base material layer of Trial Production Example 1 was changed from resin B1 to resin B2, and the amount of resin A1 was set to 85% by weight and the amount of resin B2 was set to 5% by weight in the base material layer.

[0081] [Trial Production Example 6]

Trial Production Example 6 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the recycled raw material in the base material layer was changed from resin B1 to resin B2.

[0082] [Trial Production Example 7]

Trial Production Example 7 is a film obtained by film formation under the same conditions as in Trial Production Example 2, except that the recycled raw material in the base material layer was changed from resin B1 to resin B2.

[0083] [Trial Production Example 8]

Trial Production Example 8 is a film obtained by film formation under the same conditions as in Trial Production Example 3, except that the recycled raw material in the base material layer was changed from resin B1 to resin B2.

[0084] [Trial Production Example 9]

Trial Production Example 9 is a film obtained by film formation under the same conditions as in Trial Production Example 4, except that the recycled raw material in the base material layer was changed from resin B1 to resin B2.

[0085] [Trial Production Example 10]

Trial Production Example 10 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the polypropylene resin in the base material layer of Trial Production Example 1 was changed from resin A1 to resin A2, and that 2% by weight of resin C1, which is a propylene- α -olefin random copolymer, was compounded in the base material layer and the amount of resin A2 was set to 78% by weight.

[0086] [Trial Production Example 11]

Trial Production Example 11 is a film obtained by film formation under the same conditions as in Trial Production Example 10, except that the thickness of the film was set to 18 μm .

[0087] [Trial Production Example 12]

Trial Production Example 12 is a film obtained by film formation under the same conditions as in Trial Production Example 10, except that the amount of resin A2 was set to 68% by weight and the amount of resin B1 was set to 20% by weight in the base material layer, and the thickness of the film was set to 16 μm .

[0088] [Trial Production Example 13]

Trial Production Example 13 is a film obtained by film formation under the same conditions as in Trial Production Example 10, except that 15% by weight of resin A3, which is a polypropylene resin, was compounded in the base material layer, and the amount of resin A2 was set to 58% by weight and the amount of resin B1 was set to 15% by weight.

[0089] [Trial Production Example 14]

Trial Production Example 14 is a film obtained by film formation under the same conditions as in Trial Production Example 10, except that the polypropylene resin in the base material layer of Trial Production Example 10 was changed from resin A2 to resin A1 and the recycled raw material was changed from resin B1 to resin B3, and that the amount of resin A1 was set to 83% by weight and the amount of resin B3 was set to 5% by weight in the base material layer.

[0090] [Trial Production Example 15]

Trial Production Example 15 is a film obtained by film formation under the same conditions as in Trial

Production Example 14, except that the amount of resin A1 was set to 78% by weight and the amount of resin B3 was set to 10% by weight in the base material layer.

[0091] [Trial Production Example 16]

Trial Production Example 16 is a film obtained by film formation under the same conditions as in Trial Production Example 14, except that the amount of resin A1 was set to 68% by weight and the amount of resin B3 was set to 20% by weight in the base material layer.

[0092] [Trial Production Example 17]

Trial Production Example 17 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that no recycled raw material was compounded in the base material layer, and 87% by weight of resin A1, 3% by weight of resin C1, and 10% by weight of resin D1 were compounded.

[0093] [Trial Production Example 18]

Trial Production Example 18 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the amount of resin A1 was set to 87% by weight and the amount of resin B1 was set to 3% by weight in the base material layer.

[0094] [Trial Production Example 19]

Trial Production Example 19 is a film obtained by film formation under the same conditions as in Trial Production Example 5, except that the amount of resin A1

was set to 60% by weight and the amount of resin B2 was set to 30% by weight in the base material layer.

[0095] [Trial Production Example 20]

Trial Production Example 20 is a film obtained by film formation under the same conditions as in Trial Production Example 2, except that the recycled raw material in the base material layer was changed from resin B1 to resin B4.

[0096] [Trial Production Example 21]

Trial Production Example 21 is a film obtained by film formation under the same conditions as in Trial Production Example 3, except that the recycled raw material in the base material layer was changed from resin B1 to resin B4.

[0097] [Trial Production Example 22]

Trial Production Example 22 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that no recycled raw material was compounded in the base material layer, and 90% by weight of resin A3 was compounded.

[0098] [Trial Production Example 23]

Trial Production Example 23 is a film obtained by film formation under the same conditions as in Trial Production Example 1, except that the propylene resin in the base material layer was changed from resin A1 to resin A3.

[0099] [Trial Production Example 24]

Trial Production Example 24 is a film obtained by film formation under the same conditions as in Trial Production Example 14, except that the amount of resin A1 was set to 58% by weight and the amount of resin B3 was set to 30% by weight in the base material layer.

[0100] [Table 1]

		Trial Production Example 1	Trial Production Example 2	Trial Production Example 3	Trial Production Example 4	Trial Production Example 5	Trial Production Example 6
First surface layer	Resin A3	100	100	100	100	100	100
Base material layer	Resin A1	80	75	70	65	85	80
	Resin A2						
	Resin A3						
	Resin B1	10	15	20	25		
	Resin B2					5	10
	Resin B3						
	Resin B4						
	Resin C1						
	Resin D1	10	10	10	10	10	10
Second surface layer	Resin A3	100	100	100	100	100	100
Film thickness (μm)		20	20	20	20	20	20

[0101] [Table 2]

		Trial Production Example 7	Trial Production Example 8	Trial Production Example 9	Trial Production Example 10	Trial Production Example 11	Trial Production Example 12
First surface layer	Resin A3	100	100	100	100	100	100
Base material layer	Resin A1	75	70	65			
	Resin A2				78	78	68
	Resin A3						
	Resin B1				10	10	20
	Resin B2	15	20	25			
	Resin B3						
	Resin B4						
	Resin C1				2	2	2
	Resin D1	10	10	10	10	10	10
Second surface layer	Resin A3	100	100	100	100	100	100
Film thickness (μm)		20	20	20	20	18	16

[0102] [Table 3]

		Trial Production Example 13	Trial Production Example 14	Trial Production Example 15	Trial Production Example 16	Trial Production Example 17	Trial Production Example 18
First surface layer	Resin A3	100	100	100	100	100	100
Base material layer	Resin A1		83	78	68	87	87
	Resin A2	58					
	Resin A3	15					
	Resin B1	15					3
	Resin B2						
	Resin B3		5	10	20		
	Resin B4						
	Resin C1	2	2	2	2	3	
	Resin D1	10	10	10	10	10	10
Second surface layer	Resin A3	100	100	100	100	100	100
Film thickness (μm)		20	20	20	20	20	20

[0103] [Table 4]

		Trial Production Example 19	Trial Production Example 20	Trial Production Example 21	Trial Production Example 22	Trial Production Example 23	Trial Production Example 24
First surface layer	Resin A3	100	100	100	100	100	100
Base material layer	Resin A1	60	75	70			58
	Resin A2						
	Resin A3				90	80	
	Resin B1					10	
	Resin B2	30					
	Resin B3						30
	Resin B4		15	20			
	Resin C1						2
	Resin D1	10	10	10	10	10	10
Second surface layer	Resin A3	100	100	100	100	100	100
Film thickness (μm)		20	20	20	20	20	20

[0104] As the performance of the biaxially oriented polypropylene films of Trial Production Examples 1 to 24, haze, heat shrinkage rate, tensile elastic modulus, degree of dimensional stability, and film formability were each evaluated. The results and evaluations of each test are shown in Tables 5 to 8 below, together with the physical properties of the recycled raw materials in each Trial Production Example.

[0105] [Haze]

Haze (%) is an index of transparency, and measurement was carried out using a haze meter (NDH-8000, manufactured by Nippon Denshoku Industries Co., Ltd.) by the test method in accordance with JIS K 7136 (2000). In the biaxially oriented polypropylene films of Trial Production Examples 1 to 24, a haze value of 5.0% or less was determined as a good product in terms of the transparency required for packaging films.

[0106] [Heat Shrinkage Rate]

The heat shrinkage rate (%) was measured based on the heating shrinkage rate test in accordance with JIS Z 1712 (2009). In this test, test pieces (15 mm in width and 150 mm in length) were cut out from the films of Trial Production Examples 1 to 24, gauge marks were placed at 100 mm intervals at the center of the sample, and a heating treatment was carried out at 150°C for 5 minutes. After heating, the length between the gauge marks in the machine (MD) direction and the transverse (TD) direction of the test piece was measured. From the measured lengths in the machine and transverse directions after heating, the proportion of change relative to the lengths in the machine and transverse directions before heating was calculated as the heat shrinkage rate (%). In terms of the heat shrinkage rate (%), 10% or less was determined as a good product.

[0107] [Tensile Elastic Modulus]

As for the tensile elastic modulus (GPa), based on the test method for tensile characteristics of plastics in accordance with JIS K 7127 (1999), test pieces of 15 mm × 200 mm were cut out from the films obtained in Trial Production Examples 1 to 24, using a tensile testing machine (RTF-1310, manufactured by Orientec Co., Ltd.). Next, based on the test method for tensile characteristics of plastics in accordance with JIS K 7127 (1999), the tensile elastic modulus in each of the machine (MD) direction and the transverse (TD) direction of the above films was measured using the tensile testing machine (RTF-1310, manufactured by Orientec Co., Ltd.) under the conditions of a distance between chucks of 100 mm and a tensile speed of 200 mm/min. In the measurement results, in the case where an elastic modulus in the machine (MD) direction of 2.0 GPa or more and an elastic modulus in the transverse (TD) direction of 4.0 GPa or more were both satisfied, the film was determined as a good product.

[0108] [Degree of Dimensional Stability]

Each of the dimensional change rates (%) at 120°C and 140°C in the machine (MD) direction was calculated according to the procedure described later using a thermomechanical analyzer (Q400, manufactured by TA Instruments Japan Inc.), and the difference between the obtained dimensional change rate at 140°C (L_{140}) and the dimensional change rate at 120°C (L_{120}), ($L_{140} - L_{120}$), was

determined as the degree of dimensional stability. In the case where the degree of dimensional stability was 15 or less, the film was determined as a good product.

[0109] For the measurement of the dimensional change rate, test pieces (4 mm in width and 25 mm in length) were cut out from the films of Trial Production Examples 1 to 24 in the machine (MD) direction. The test piece was set on the sample holder so that the distance between the chucks was about 8 mm, with the machine (MD) direction as the tensile direction, and fixed to the probe of the thermomechanical analyzer. The length of the test piece before heating (L_0) under a load of 0.32 N applied to the test piece was read. While applying a load of 0.32 N in the machine direction of the test piece, the temperature was raised from 30°C to 150°C at a temperature rise rate of 20°C/min, and the length of the test piece in the machine (MD) direction when reaching 120°C (L_1) and the length of the test piece in the machine (MD) direction when reaching 140°C (L_2) were each read. The lengths of the test piece before and after heating (L_0), (L_1), and (L_2) were substituted into the following expressions (iii) and (iv), and the dimensional change rate at 120°C (L_{120}) and the dimensional change rate at 140°C (L_{140}) were calculated from the relationship between the length of the test piece before heating and the amount of change.

$$L_{120} (\%) = \{(L_1 - L_0)/L_0\} \times 100 \dots (iii)$$

$$L_{140} (\%) = \{(L_2 - L_0)/L_0\} \times 100 \dots (iv)$$

[0110] [Film Formability]

For the determination of film formability, during film formation of the films of Trial Production Examples 1 to 24, appearance defects such as uneven stretching were visually checked, and a good appearance was determined as "Good", while the presence of appearance defects was determined as "Poor".

[0111] [Table 5]

		Trial Production Example 1	Trial Production Example 2	Trial Production Example 3	Trial Production Example 4	Trial Production Example 5	Trial Production Example 6
Recycled raw material	Amount added (%)	10.0	15.0	20.0	25.0	5.0	10.0
	MFR (g/min)	5.4	5.4	5.4	5.4	5.7	5.7
	Melting peak temperature (°C)	162	162	162	162	161	161
	Melting enthalpy (J/g)	100.2	100.2	100.2	100.2	100.5	100.5
	Crystallization temperature (°C)	112	112	112	112	114	114
	Mw/Mn	4.3	4.3	4.3	4.3	4.3	4.3
	Mz+1/Mw	5.0	5.0	5.0	5.0	4.8	4.8
Haze (%)		1.4	1.3	1.3	1.3	1.2	1.4
Heat shrinkage rate	MD	4.4	4.8	5.0	4.7	5.1	4.7
	TD	2.9	3.2	3.3	2.9	3.5	4.0
Tensile elastic modulus (GPa)	MD	2.4	2.4	2.5	2.5	2.5	2.4
	TD	4.9	4.9	4.8	4.9	5.0	4.8
Degree of dimensional stability	L ₁₂₀ (%)	4.3	4.6	4.0	4.5	3.8	4.1
	L ₁₄₀ (%)	11.8	12.2	11.3	12.5	11.0	9.8
	L ₁₄₀ -L ₁₂₀	7.5	7.7	7.3	8.0	7.3	5.6
Film formability		Good	Good	Good	Good	Good	Good

[0112] [Table 6]

		Trial Production Example 7	Trial Production Example 8	Trial Production Example 9	Trial Production Example 10	Trial Production Example 11	Trial Production Example 12
Recycled raw material	Amount added (%)	15.0	20.0	25.0	10.0	10.0	20.0
	MFR (g/min)	5.7	5.7	5.7	5.4	5.4	5.4
	Melting peak temperature (°C)	161	161	161	162	162	162
	Melting enthalpy (J/g)	100.5	100.5	100.5	100.2	100.2	100.2
	Crystallization temperature (°C)	114	114	114	112	112	112
	Mw/Mn	4.3	4.3	4.3	4.3	4.3	4.3
	Mz+1/Mw	4.8	4.8	4.8	5.0	5.0	5.0
Haze (%)		1.5	1.4	1.5	1.2	1.7	0.9
Heat shrinkage rate	MD	4.5	5.1	5.0	4.0	4.1	7.9
	TD	2.5	3.2	3.0	2.1	2.2	6.4
Tensile elastic modulus (GPa)	MD	2.4	2.5	2.4	2.3	2.3	2.2
	TD	4.8	4.8	4.6	4.8	4.7	4.1
Degree of dimensional stability	L ₁₂₀ (%)	4.0	4.2	5.3	4.5	4.8	6.6
	L ₁₄₀ (%)	10.9	12.1	15.6	12.8	13.4	21.0
	L ₁₄₀ -L ₁₂₀	6.8	7.9	10.3	8.3	8.5	14.4
Film formability		Good	Good	Good	Good	Good	Good

[0113] [Table 7]

		Trial Production Example 13	Trial Production Example 14	Trial Production Example 15	Trial Production Example 16	Trial Production Example 17	Trial Production Example 18
Recycled raw material	Amount added (%)	15.0	5.0	10.0	20.0	0.0	3.0
	MFR (g/min)	5.4	10.1	10.1	10.1	-	5.4
	Melting peak temperature (°C)	162	150	150	150	-	162
	Melting enthalpy (J/g)	100.2	87.6	87.6	87.6	-	100.2
	Crystallization temperature (°C)	112	117	117	117	-	112
	Mw/Mn	4.3	4.6	4.6	4.6	-	4.3
	Mz+1/Mw	5.0	4.9	4.9	4.9	-	5.0
Haze (%)		1.0	1.0	1.9	2.4	1.1	1.4
Heat shrinkage rate	MD	7.4	5.3	5.2	5.6	4.7	4.5
	TD	4.6	4.8	4.2	2.2	2.8	3.5
Tensile elastic modulus (GPa)	MD	2.2	2.2	2.1	2.0	2.6	2.5
	TD	4.2	4.8	4.7	4.2	5.0	5.0
Degree of dimensional stability	L ₁₂₀ (%)	5.5	3.4	3.6	4.3	3.7	4.2
	L ₁₄₀ (%)	17.1	8.0	8.6	10.8	11.7	11.9
	L ₁₄₀ -L ₁₂₀	11.6	4.6	5.0	6.5	7.9	7.8
Film formability		Good	Good	Good	Good	Good	Good

[0114] [Table 8]

		Trial Production Example 19	Trial Production Example 20	Trial Production Example 21	Trial Production Example 22	Trial Production Example 23	Trial Production Example 24
Recycled raw material	Amount added (%)	30.0	15.0	20.0	0.0	10.0	30.0
	MFR (g/min)	5.7	10.1	10.1	-	5.4	10.1
	Melting peak temperature (°C)	161	140	140	-	162	150
	Melting enthalpy (J/g)	100.5	86.8	86.8	-	100.2	87.6
	Crystallization temperature (°C)	114	102	102	-	112	117
	Mw/Mn	4.3	4.8	4.8	-	4.3	4.6
	Mz+1/Mw	4.8	4.6	4.6	-	5.0	4.9
Haze (%)		1.6	2.3	2.5	0.9	1.1	2.5
Heat shrinkage rate	MD	4.9	5.2	5.8	6.3	6.4	6.8
	TD	3.1	2.1	2.4	4.9	4.2	0.7
Tensile elastic modulus (GPa)	MD	2.4	2.2	2.3	2.2	2.1	1.9
	TD	4.5	3.9	3.9	3.9	4.0	3.7
Degree of dimensional stability	L ₁₂₀ (%)	5.2	4.6	7.2	7.2	8.0	6.2
	L ₁₄₀ (%)	20.2	12.7	28.7	23.3	28.9	17.6
	L ₁₄₀ -L ₁₂₀	15.1	8.1	21.5	16.1	20.9	11.4
Film formability		Good	Good	Good	Good	Good	Good

[0115] [Results and Discussion]

Trial Production Example 17 is a biaxially oriented polypropylene film having a resin composition that is mainly composed of a highly crystalline polypropylene resin (resin A1) and contains no recycled raw material. As shown in Table 7, Trial Production Example 17 exhibits good film performance overall in terms of haze, heat shrinkage rate, tensile elastic modulus, degree of dimensional stability, and film formability. It is preferable that other films containing recycled raw materials have film performance equivalent to that of the film of Trial Production Example 17.

[0116] Trial Production Examples 1 to 4 and 18 are examples in which a highly crystalline polypropylene resin (resin A1) was used as the main raw material of the base material layer, and resin B1 was used as the recycled raw material, with its compounding amount adjusted. Similarly, Trial Production Examples 5 to 9 and 19 are examples in which resin B2 was used as the recycled raw material, with its compounding amount adjusted. Trial Production Examples 14 to 16 and 24 are examples in which resin B3 was used as the recycled raw material, with its compounding amount adjusted. Trial Production Examples 20 and 21 are examples in which resin B4 was used as the recycled raw material, with its compounding amount adjusted.

[0117] In the respective films of the above Trial Production Examples, the films in which sufficient film

performance was not obtained were Trial Production Examples 19 to 21 and 24. When the films of Trial Production Examples 19 and 24 are compared with the other films in which good film performance was obtained, the films of Trial Production Examples 19 and 24 contained an excessive amount of recycled raw material compared with the other films. On the other hand, Trial Production Examples 20 and 21 had a compounding proportion of recycled raw material equivalent to that of the films with good film performance. From these results, it is considered that the physical properties of resin B4, which was compounded in Trial Production Examples 20 and 21, are not preferable as the recycled raw material.

[0118] Accordingly, from a comparison between the physical properties of the recycled raw materials (resins B1, B2, and B3), which gave good results, and the physical properties of the recycled raw material of resin B4, it is considered that preferable physical properties of the recycled raw material are as follows: the MFR is 11.0 g/10 min or less; the melting peak temperature is 145°C or higher; the melting enthalpy is 87.0 J/g or more; and the crystallization temperature is 105°C or higher. Among these physical properties, the lower limit of the MFR is considered to be about 3 g/10 min in consideration of the fluidity of the resin. The upper limit of the melting peak temperature is considered to be about 170°C in consideration of practically usable resin

molded articles. Moreover, in the recycled raw material, from a comparison between resins B1, B2, and B3 and resin B4, it is considered preferable that the molecular weight distribution (M_w/M_n and M_{z+1}/M_w) determined by GPC measurement satisfies the relationship of $M_w/M_n < M_{z+1}/M_w$, as well as $M_{z+1}/M_w \geq 4.7$.

[0119] Next, a preferable compounding proportion of the recycled raw material is studied. Trial Production Example 19 (resin B2) and Trial Production Example 24 (resin B3) are considered to have had an excessive compounding proportion. Accordingly, from Trial Production Examples 1 to 4 and 18 (resin B1), Trial Production Examples 5 to 9 (resin B2), and Trial Production Examples 14 to 16 (resin B3), which gave good results, the preferable compounding proportion of the recycled raw material is considered to be 25% by weight or less. Taking also the viewpoint of environmental burden reduction into consideration, it is preferable that the recycled raw material is contained in a compounding proportion of about 5% by weight. Therefore, the preferable compounding proportion of the recycled raw material by which both good film performance and contribution to the environment are achieved is considered to be about 5 to 25% by weight.

[0120] Trial Production Example 10 is a film in which, compared to Trial Production Example 1, the main raw material of the base material layer was changed to

another highly crystalline polypropylene resin (resin A2), and a propylene- α -olefin random copolymer (resin C1) was compounded. In Trial Production Example 10, film performance almost equivalent to that of Trial Production Example 1 was obtained. Thus, even when a small amount of a propylene- α -olefin random copolymer was compounded in the base material layer, deterioration of film performance was not observed. The propylene- α -olefin random copolymer can be added in such a compounding amount that the compounding amount of the propylene resin is not reduced, and 10% by weight or less is considered preferable, for example.

[0121] Moreover, Trial Production Examples 11 to 13 are films in which partial modifications were made to the film of Trial Production Example 10. Trial Production Example 11 is a film with reduced thickness. Trial Production Example 12 is a film with increased recycled raw material (resin B1). Trial Production Example 13 is a film in which a small amount of a low-crystalline polypropylene resin (resin A3) was added to the base material layer. In all of Trial Production Examples 11 to 13, good film performance was obtained. From Trial Production Example 11, it is considered that thickness adjustment within the range required for the film does not cause a significant change in film performance. From Trial Production Example 12, it was found that, even in a film in which a small amount of the propylene- α -olefin

random copolymer is compounded in the base material layer, good film performance can be obtained even when the compounding amount of recycled raw material is increased within the range of 5 to 25% by weight. From Trial Production Example 13, it was found that good film performance can be obtained even when a small amount of the low-crystalline polypropylene resin is contained in the base material layer mainly composed of the highly crystalline polypropylene resin.

[0122] For the study of the main raw material polypropylene resin, in Trial Production Example 22, a low-crystalline polypropylene resin (resin A3) was used as the main raw material and a biaxially oriented polypropylene film containing no recycled raw material was produced. In the film of Trial Production Example 22, the tensile elastic modulus in the transverse (TD) direction was insufficient, and the required stiffness was not obtained; furthermore, the degree of dimensional stability was also inadequate. This is considered to be due to the low crystallinity of the polypropylene resin, which resulted in deterioration of stiffness, heat resistance, and other properties of the film.

[0123] Moreover, Trial Production Example 23 is a film based on Trial Production Example 22, with 10% by weight of resin B1 compounded as the recycled raw material. It corresponds to a film in which the highly crystalline polypropylene resin (resin A1) in the base material layer

of Trial Production Example 1 is changed to the low-crystalline polypropylene resin (resin A3). In Trial Production Example 23, the degree of dimensional stability was inadequate. This is considered to be due to the low crystallinity of the polypropylene resin, as in Trial Production Example 22, which resulted in deterioration of heat resistance and other properties, indicating that the crystallinity of the polypropylene resin, which is the main raw material of the film, influenced the film performance regardless of the presence or absence of recycled raw material.

[0124] Based on the evaluation of the above Trial Production Examples, it was shown that, in films containing recycled raw materials, as conditions in order not to impair the following performance: the elastic modulus in the machine direction and the transverse direction; the degree of dimensional stability (the difference between the dimensional change rate at 140°C and the dimensional change rate at 120°C in the machine direction); and the heat shrinkage rate in the machine direction and the transverse direction, it is preferable that the main raw material of the base material layer is 55% by weight or more of a highly crystalline polypropylene resin having a mesopentad fraction of 95% or more, and that the recycled raw material satisfies all of the following: a MFR of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C, and a melting

enthalpy of 87.0 J/g or more, with a compounding proportion of 5 to 25% by weight. It was also shown that, even in the case where a propylene- α -olefin random copolymer is compounded, film performance is not impaired if the amount is about 10% by weight or less.

Industrial Applicability

[0125] In the biaxially oriented polypropylene film of the present invention, by using a recycled raw material that satisfies all of the following: melt flow rate, and melt flow rate, melting peak temperature, and melting enthalpy under predetermined conditions, excellent film formability can be obtained without impairing film performance such as stiffness or heat resistance. Therefore, it is possible to provide a biaxially oriented polypropylene film that can contribute to environmental burden reduction, and a laminate using this film, which is promising as an alternative to conventional biaxially oriented polypropylene films and their laminates.

Claims

[Claim 1]

A biaxially oriented polypropylene film which is a laminated film comprising a base material layer and a surface layer laminated on one side or each of both sides of the base material layer,

the base material layer containing a recycled raw material derived from a molded article mainly composed of a polypropylene resin, the laminated film having:

an elastic modulus in a machine (MD) direction of 2.0 GPa or more and an elastic modulus in a transverse (TD) direction of 4.0 GPa or more, as measured in accordance with JIS K 7127 (1999);

a difference between a dimensional change rate at 140°C in the machine (MD) direction, L_{140} (%), and a dimensional change rate at 120°C, L_{120} (%), $(L_{140} - L_{120})$, of 15 or less, as measured with a thermomechanical analyzer (TMA) with a temperature rise from 30°C to 150°C at 20°C/min under a load of 0.32 N applied in the machine (MD) direction; and

a heat shrinkage rate of 10% or less in each of the machine (MD) direction and the transverse (TD) direction in a heating treatment at 150°C for 5 minutes,

wherein the base material layer is formed of a resin mixture in which at least two or more different resins are mixed, including:

55% by weight or more of a polypropylene resin (A) having a mesopentad fraction (mmmm) of 95% or more; and

5 to 25% by weight of the recycled raw material (B) having a melt flow rate (MFR) of 3.0 to 11.0 g/10 min, a melting peak temperature of 145 to 170°C, as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012), and a melting enthalpy (ΔH) of 87.0 J/g or more.

[Claim 2]

The biaxially oriented polypropylene film according to claim 1, wherein the recycled raw material (B) has a crystallization temperature of 105°C or higher, as measured with a differential scanning calorimeter (DSC) in accordance with JIS K 7122 (2012).

[Claim 3]

The biaxially oriented polypropylene film according to claim 1 or 2, wherein a relationship of molecular weight distribution (M_w/M_n and M_{z+1}/M_w) of the recycled raw material (B), as determined by gel permeation chromatography (GPC) measurement, satisfies $M_w/M_n < M_{z+1}/M_w$ and $M_{z+1}/M_w \geq 4.7$.

M_w : weight average molecular weight

M_n : number average molecular weight

M_{z+1} : Z+1 average molecular weight

[Claim 4]

The biaxially oriented polypropylene film according to claim 1 or 2, wherein the base material layer contains

10% by weight or less of a propylene- α -olefin random copolymer (C).

[Claim 5]

The biaxially oriented polypropylene film according to claim 3, wherein the base material layer contains 10% by weight or less of a propylene- α -olefin random copolymer (C).

[Claim 6]

A laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to claim 1 or 2.

[Claim 7]

A laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to claim 3.

[Claim 8]

A laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to claim 4.

[Claim 9]

A laminate in which a sealant film is laminated on the biaxially oriented polypropylene film according to claim 5.

[Claim 10]

The laminate according to claim 6, wherein the sealant film is a cast polypropylene film.

[Claim 11]

The laminate according to claim 7, wherein the sealant film is a cast polypropylene film.

[Claim 12]

The laminate according to claim 8, wherein the sealant film is a cast polypropylene film.

[Claim 13]

The laminate according to claim 9, wherein the sealant film is a cast polypropylene film.