

TITLE

Biaxially oriented polypropylene film, method for preparing the same and use thereof.

FIELD OF THE INVENTION

The present invention relates to a biaxial oriented polypropylene film with excellent heat resistance and high clarity. The present invention relates further to a method for preparing the biaxial oriented polypropylene film, a multilayer film or an article comprising the biaxial oriented polypropylene film, and the use of the biaxial oriented polypropylene film.

BACKGROUND OF THE INVENTION

In the recent years, a dramatically increase in the demand for mono-material flexible packaging has led to a replacement of polyester (poly(ethylene terephthalate) or PET) and/or polyamide (Nylon) in multilayer lamination with polyolefin. For polypropylene (PP)-based mono-material packaging, several attempts have been made to develop a biaxial oriented polypropylene (BOPP) film with higher heat resistance. This enhanced feature improves machinability of the PP-based mono-material structure, especially at high speed packaging machines, as compared to a conventional BOPP film.

TH1001001007 discloses thin and clarity biaxially oriented film comprising a homopolypropylene or a copolymer polypropylene or a polypropylene blend with polyethylene content of less than 50% and a beta-nucleating agent with a particle size less than 0.1 μm and a content 0.1-100 ppm. The polypropylene has a MFR of 1-10 g/10 min

CN 106674745 A discloses a biaxially-oriented polypropylene film suitable for hot pressing technology of printed circuit boards. The film comprises an upper surface layer, a core layer and a lower surface layer. The film comprises 954 to 979 parts of homopolypropylene, 20 to 45 parts of nucleating agent, and 1 to 2 parts of anti-blocking agent.

WO 2013/097647 A1 discloses a β -crystal form nucleating agent composition for polypropylene preparation which contains a carboxylic acid metal salt of a β -crystal form nucleating agent, tetrahydrophthalic anhydride and an auxiliary agent chosen from calcium carbonate, hydrotalcite and talc powder. The nucleating agent composition provides polypropylene having improved impact strength by up to 6 times, the heat distortion temperature is improved by about 10 to 20 $^{\circ}\text{C}$, and rigidity. The composition comprises 5-95 wt% carboxylic acid metal salt of tetrahydrophthalic anhydride in a concentration of 0.05-0.5 wt% of polypropylene and 5-95 wt% adjuvant being selected from the group consisting of calcium carbonate, hydrotalcite and talc powder. The polypropylene homopolypropylene or an ethylene propylene copolymer is a polypropylene tube material having a melt flow rate of 0.2 to 0.5 g/10 min, or melted. Polypropylene with a body flow rate of 2-15 g/10 min.

US 2018/0265671 A1 discloses a biaxially oriented polypropylene film comprising at least one layer that comprises a nucleating agent, a potassium salt of a fatty acid, and a thermoplastic essentially consisting of polypropylene, wherein the films contain low levels of nucleating agent (e.g. less than 10 ppm), and all of the thermoplastics in the layer of the film essentially consist of polypropylene.

US 6,733,719 B2 discloses a method of making a polypropylene product providing an extrusion grade mini-random polypropylene; combining the extrusion grade polypropylene with a non-particulate nucleation system to form a composition; and processing the composition into the product. The concentration of nucleating system is 25-300 ppm. Preferably, the nucleating system comprises a blend of a monocarboxylic acid nucleating agent and dicarboxylic acid nucleating agent.

TECHNICAL PROBLEM

However, there is still a need for biaxially orientation polypropylene film with improved properties.

It is the object of the present invention to provide a biaxially orientation polypropylene film with excellent heat resistance, high clarity and good sealing performance.

TECHNICAL SOLUTION

The object is achieved by a biaxially oriented polypropylene film comprising a composition comprising a polypropylene and a beta-nucleating agent, wherein

- the biaxially oriented polypropylene film has a porosity calculated according to the following formula of less than 0.01, , alternatively 0.001, alternatively 0.0001, alternatively 0.00001, alternatively about 0-0.00001,

$$\text{Porosity} = [1 - (d_1/d_0)] \cdot 100$$

wherein

d_1 is the density of the biaxially oriented polypropylene film after stretching,
and

d_0 is the density of the biaxially oriented polypropylene film before stretching;
and

- the composition has a crystallization half-time at 136°C in the range of 1 to 10 min, preferably 2-6 min determined by differential scanning calorimetry under isothermal conditions, and a MFR₂ of 2-10 g/10 min, preferably 2-5 g/10 min determined according to ASTM D-1238-13 at 230 °C 2.16 kgf, and

- the polypropylene has a tacticity from 93 to 99 %, preferably 94 to 98 %.

The polypropylene may be homopolypropylene or random copolymer polypropylene having ethylene content not more than 0.5 mol%, preferably homopolypropylene. The polypropylene may be homopolypropylene and may have a tacticity from 93 to 99 %, preferably 94 to 98 %, more preferably 94-97 %.

The composition may have an MFR₂ of 2-10 g/10 min, preferably 2-5 g/10 min.

The beta-nucleating agent may be selected from the group consisting of a metal phthalate, a metal salt, a metal hydrophthalate, dicarboxylic acid derivative type diamide compounds from C₅-C₈-cycloalkyl monoamines or C₆-C₁₂-aromatic monoamines and C₅-C₈-aliphatic, C₅-C₈-cycloaliphatic or C₆-C₁₂-aromatic dicarboxylic acids or mixtures thereof, preferably a calcium salt, most preferred calcium tetrahydrophthalate or the commercially available product MPM 2000 from Mayzo.

The beta-nucleating agent may be contained in the composition in an amount from 250 to 1,500 ppm by weight, alternatively 500 to 1,250 ppm by weight, alternatively 500 to 1,250 ppm by weight, alternatively 700 to 1,200 ppm by weight, alternatively 900 to 1,100 ppm by weight with respect to the total weight of the composition.

The composition may further comprise at least one additive, preferably selected from an antioxidant, a neutralizer, an inorganic filler, an organic filler or mixtures thereof.

The composition may have a melt flow rate of 2 to 10 g/10 min, preferably 2 to 5 g/10 min determined according to ASTM D-1238-13 at 230 °C 2.16 kgf.

The biaxially oriented polypropylene film may have a thickness in the range of 20-30 µm has OTR at 23 °C and 0 %RH of less than 10000 cc/m².day, preferably in the range of 500-5000 cc/m².day, most preferably 1000-3000 cc/m².day, according to ASTM D3985; and a WVTR at 38 °C and 90 %RH in the range of 1-20 g/m² · day, preferably 1-10 g/m² · day according to ASTM F1249.

The biaxially oriented polypropylene film may have a lamella thickness (Lc) of more than 22 nm, preferably from 22 to 60 nm, preferably 22-40 nm, most preferably 22-30 nm.

The biaxially oriented polypropylene film may have a thermal shrinkage by placing a 10x10 cm² sample of the biaxially oriented polypropylene film into hot-air oven at 120°C, 15 min in machine direction (MD) from 0 to 5 %, preferably 0-2% and transverse direction (TD) from 0 to 5 %, preferably 0-2%

The biaxially oriented polypropylene film may have a melt temperature (T_m) of film at least 170°C, preferably 170-175°C.

The biaxially oriented polypropylene film may have a haze of less than 7% (ASTM D-1003) measured on a thickness of 20 μm , preferably has a haze of 1-6%, most preferably 1-3%.

The biaxially oriented polypropylene film may have a specific heat capacity (C_p) at 145 $^{\circ}\text{C}$ in the range of 1-5 J/g.K, preferably 3-3.8 J/g.K.

The biaxially oriented polypropylene film may have a thickness in the range from 10 to 100 μm , preferably 10 to 70 μm , most preferably 10 to 50 μm .

The object is further achieved by a method for preparing the biaxially oriented polypropylene film according to the invention comprising the steps:

- mixing the polypropylene and the beta-nucleating agent to form pellets;
- extruding the pellets to form a film;
- casting the film with a chill roll temperature in the range of 30-70 $^{\circ}\text{C}$, preferably 40-60 $^{\circ}\text{C}$; and
- stretching and annealing the film in machine direction and transverse direction to form the biaxially oriented polypropylene film.

The object is further achieved by a multilayer film comprising the biaxially oriented polypropylene film according to the invention.

The object is further achieved by an article comprising the biaxially oriented polypropylene film according to the invention.

The object is further achieved by a use of the biaxially oriented polypropylene film according to the invention in a packaging.

DEFINITIONS

As used herein, the term “ β -nucleating agent” refers to a chemical substance that aids the crystallisation of a polypropylene into a crystalline polypropylene primarily containing the β -crystal form.

As used herein, the term "biaxially oriented film" is film stretched in both machine and transverse direction causing molecular chain orientation in two directions.

As used herein, the term “homopolypropylene” refers to a polymer which consists essentially of repeat units deriving from propylene, for example, comprises at least 99%, more preferably at least 99.5%, still more preferably at least 99.95%, and yet more preferably at least 99.95% e.g. 100%, by weight of repeat units deriving from propylene.

As used herein, the term “molecular weight distribution” (MWD) refers to the ratio of the weight average molecular weight (Mw) of a polymer to its number average molecular weight (Mn), i.e. (Mw/Mn).

As used herein, the term “tacticity” describes how the methyl group is oriented in the polymer chain. For isotactic polypropylene, the methyl group is evenly aligned at the same side.

As used herein, the term “Lamella thickness” refers to the thickness of the lamella or regular crystalline structure. During the crystallization, the polymer chains rearrange to form regular crystalline structure or lamellar structure which consists of tightly packed and folded polymers chain. Lamella thickness refers to the thickness of this lamellar structure.

Unless the context requires otherwise, throughout the specification and claims that follow, the word “comprise” and variations thereof, such as “comprises” and “comprising” are to be construed in an open, inclusive sense, that is, as “including, but not limited to”.

DETAILED DESCRIPTION OF THE INVENTION

The invention provides a biaxially oriented polypropylene film comprising a composition comprising a polypropylene and a beta-nucleating agent, wherein

- the biaxially oriented polypropylene film has a porosity calculated according to the following formula of less than 0.01, alternatively 0.001, alternatively 0.0001, alternatively 0.00001, alternatively about 0 to 0.00001.

$$\text{Porosity} = [1 - (d_i/d_o)] \cdot 100$$

wherein

d_i is the density of the biaxially oriented polypropylene film after stretching, and

d_o is the density of the biaxially oriented polypropylene film before stretching;

- The composition has a crystallization half-time at 136°C in the range of 1 to 10 min, preferably 2-6 min determined by differential scanning calorimetry under isothermal conditions, and a MFR₂ 2-10 g/10 min,

preferably 2-5 g/10 min determined according to ASTM D-1238-13 at 230 °C 2.16 kg, and

- the polypropylene has a tacticity from 93 to 99 %, preferably 94 to 98 %.

Polypropylene suitably, but not limited to, homopolypropylene and random copolymer ($C_2 \leq 0.5\%$ mol), preferably is homopolypropylene

The (homo)polypropylene may have a MWD in the range of 5-17, preferably 6-16 and more preferably 7-16.

The tacticity of (homo)polypropylene may be more than 93%, preferably in the range of 94-99%, and more preferably 94-98%, preferably 94-96%.

The MFR₂ of the (homo)polypropylene may be in the range of 1 – 10 g/10 min at 230 °C and 2.16 kgf, preferably 1-5 g/10 min and more preferably 2-5 g/10 min.

The composition for producing the biaxially oriented polypropylene film may have a crystallization half-time at 136°C in the range of 1 to 10, alternatively 1.5 to 8 min, alternatively 1.8 to 7 min, alternatively 2 to 6 min, determined by differential scanning calorimetry under isothermal conditions.

The MFR₂ of the composition may be in the range of 2-10 g/10 min, preferably 2-5 g/10 min determined according to ASTM D-1238-13 at 230 °C 2.16 kg.

The tacticity of the polypropylene may be more than 93%, preferably in the range of 94-98%, and more preferably 94-97%.

The beta-nucleating agent may be selected from the group consisting of a metal phthalate, a metal salt, a metal hydrophthalate, dicarboxylic acid derivative type diamide compounds from C5-C8-cycloalkyl monoamines or C6-C12-aromatic monoamines and C5-C8-aliphatic, C5-C8-cycloaliphatic or C6-C12-aromatic dicarboxylic acids or mixtures thereof. The beta-nucleating agent may be selected from the group consisting of a group II metal phthalate, a group II metal salt, a group II metal hydrophthalate or mixtures thereof.

Preferably, the metal hydrophthalate is selected from barium tetrahydrophthalate, calcium tetrahydrophthalate, 4-methylcalcium tetrahydrophthalate, magnesium tetrahydrophthalate, strontium tetrahydrophthalate, zinc tetrahydrophthalate, and aluminium tetrahydrophthalate, or mixtures thereof. More preferably, the metal hydrophthalate is selected from barium tetrahydrophthalate, calcium tetrahydrophthalate, magnesium tetrahydrophthalate, and strontium tetrahydrophthalate, or mixtures thereof.

Most preferred, the beta-nucleating agent may be calcium tetrahydrophthalate.

Preferably, the dicarboxylic acid derivative type diamide compounds from C5-C8-cycloalkyl monoamines or C6-C12-aromatic monoamines and C5-C8-aliphatic, C5-C8-cycloaliphatic or C6-C12-aromatic dicarboxylic acids are selected from N,N'-di-C5-C8-cycloalkyl-2,6-naphthalene dicarboxamide compounds such as N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide and N,N'-dicyclooctyl-2,6-naphthalene dicarboxamide, N,N'-di-C5-C8-cycloalkyl-4,4-biphenyldicarboxamide compounds such as N,N'-dicyclohexyl-4,4-biphenyldicarboxamide and N,N'-dicyclopentyl-4,4-biphenyldicarboxamide, N,N'-di-C5-C8-cycloalkyl-terephthalamide compounds such as N,N'-dicyclohexylterephthalamide and N,N'-dicyclopentylterephthalamide, N,N'-di-C5-C8-cycloalkyl-1,4-cyclohexanedicarboxamide compounds such as N,N'-dicyclohexyl-1,4-cyclohexanedicarboxamide and N,N'-dicyclohexyl-1,4-cyclopentanedicarboxamide, diamine derivative type diamide compounds from C5-C8-cycloalkyl monocarboxylic acids or C6-C12-aromatic monocarboxylic acids and C5-C8-cycloaliphatic or C6-C12-aromatic diamines, e.g. N,N'-C6-C12-arylene-bis-benzamide compounds such as N,N'-p-phenylene-bis-benzamide and N,N'-1,5-naphthalene-bis-benzamide, N,N'-C5-C8-cycloalkyl-bis-benzamide compounds such as N,N'-1,4-cyclopentane-bis-benzamide and N,N'-1,4-cyclohexane-bis-benzamide, N,N'-p-C6-C12-arylene-bis-C5-C8-cycloalkylcarboxamide compounds such as N,N'-1,5-naphthalene-bis-cyclohexanecarboxamide and N,N'-1,4-phenylene-bis-cyclohexanecarboxamide, and N,N'-C5-C8-cycloalkyl-bis-cyclohexanecarboxamide compounds such as N,N'-1,4-cyclopentane-bis-cyclohexanecarboxamide and N,N'-1,4-cyclohexane-bis-cyclohexanecarboxamide, amino acid derivative type diamide compounds from amidation reaction of C5-C8-alkyl, C5-C8-cycloalkyl- or C6-C12-aryl amino acids, C5-C8-alkyl-, C5-C8-cycloalkyl- or C6-C12-aromatic monocarboxylic acid chlorides and C5-C8-alkyl-, C5-C8-cycloalkyl- or C6-C12-aromatic mono-amines, e.g. N-phenyl-5-(N-benzoylamino)pentane amide and N-cyclohexyl-4-(N-cyclohexyl-carbonylamino)benzamide. In this regard, preferred beta-nucleating agents are any one or mixtures of N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide.

The composition may comprise the beta-nucleating agent in an amount from 250 to 1,500 ppm by weight, alternatively 500 to 1,250 ppm by weight, preferably 700 to 1,200 ppm by weight, most preferably 900 to 1,100 ppm by weight, with respect to the total weight of the composition.

The composition may further comprise at least one additive, preferably selected from an antioxidant, a neutralizer, an inorganic filler, an organic filler or mixtures thereof. The (homo)polypropylene may contain one or more additive(s) and/or other resins. The additives may be present in the composition in an amount of 1-7 wt% with respect to the total weight of the film. The additives may include an antioxidant such as Irganox 1010, Irgafos 168, a neutralizer such as calcium stearate, hydrotalcite, an inorganic or organic fillers such as silica, clay, talcum.

The biaxially oriented polypropylene film may have a thickness in the range of 20-30 μm has oxygen transmission rate (OTR) at 23 °C and 0 % room humidity (RH) of less than 10000 cc/m².day, preferably in the range of 500-5000 cc/m².day, most preferably 1000-

3000 cc/m².day, as measured according to ASTM D3985; and water vapor transmission rate (WVTR) at 38 °C and 90 %RH in the range of 1-20 g/m² · day, preferably 1-10 g/m² · day, as measured following to ASTM F1249.

The biaxially oriented polypropylene film may have a Thickness of lamellar crystalline (Lc) of more than 22 nm, alternatively from 22 to 60 nm, preferably from 22 to 40 nm, most preferably 22-30 nm.

The biaxially oriented polypropylene film may have a thermal shrinkage by placing a 10x10 cm² sample of the biaxially oriented polypropylene film into hot-air oven at 120°C, 15 min in machine direction (MD) from 0 to 5 %, preferably 0-2% and transverse direction (TD) from 0 to 5 %, preferably 0-2%.

The biaxially oriented polypropylene film has a specific heat capacity (Cp) at 145 °C in the range of 1-5 J/g.K, preferably 3-3.8 J/g.K.

The biaxially oriented polypropylene film may have a thickness in the range from 10 to 100 µm, preferably 10 to 70 µm, most preferably 10 to 50 µm.

The biaxially oriented polypropylene film may have a Tm of film of at least 170°C, preferably 170-175°C.

The biaxially oriented polypropylene film may have a haze of less than 7% (ASTM D-1003) measured on thickness 20 µm, preferably has a haze of 1-6%, most preferably 1-3%.

The composition may have a melt flow rate of 2-10 g/10 min, preferably 2-5 g/10 min determined according to ASTM D-1238-13 at 230 °C 2.16 kg.

The invention further provides a method for preparing the biaxially oriented polypropylene film according to the invention comprising the steps:

- mixing the polypropylene and the beta-nucleating agent to form pellets;
- extruding the pellets to form a film;
- casting the film with chill roll temperature in the range of 30-70 °C, preferably 40-60 °C; and
- stretching and annealing the film in machine direction and transverse direction to form the biaxially oriented polypropylene film.

A sequential or simultaneous biaxially oriented stretching process may be applied to get the biaxially oriented stretching polypropylene film.

The invention further provides a multilayer film comprising the biaxially oriented polypropylene film according to the invention.

The biaxially oriented polypropylene film may be coated with metal oxide or metallized on the film to improve the barrier property.

The invention further provides an article comprising the biaxially oriented polypropylene film according to the invention. The article may be a multilayer packaging or a laminated film.

The invention further provides a use of the biaxially oriented polypropylene film according to the invention in a packaging, preferably a multilayer film packaging.

The use of the biaxially oriented polypropylene film according to the invention provides printability.

It is one technical advantage of the biaxially oriented polypropylene film according to the invention that the same can be recycled.

Materials

Commercially available homopolypropylene purchased from SCG Chemicals was used. The melt flow rate (MFR₂) at 230 °C and 2.16 kgf of the polypropylene is 2-4 g/min and tacticity measured by pentad ratio (%mmmm) by NMR more than 94%. The polypropylene has molecular weight distribution of 8.

NAB-82 (Calcium tetrahydrophthalate) purchased from Chemsync, MPM 2000 from Mayzo, NJ Star® NU-100 (N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide) from New Japan, and PV Fast Red E3B or Hostaperm Red E5B 02 (quinacridone pigments) from Clariant were used as beta-nucleating agent.

Measurement methods

Melt flow rate (MFR₂) is determined according to ASTM D-1238-13 at 230 °C 2.16 kg.

Tacticity is determined by pentad ratio (%mmmm) by NMR spectroscopy.

Weight average molecular weight (M_w), number average molecular weight (M_n) and Molecular weight Distribution (MWD) were measured by gel permeable chromatography (GPC). Molecular weight Distribution (MWD) was calculated by Mw/Mn. Around 8 mg of sample was dissolved in 8 ml of 1,2,4-trichlorobenzene at 160°C for 90 min. Then the sample solution, 200 µl, was injected into the high temperature GPC with IR5, an infrared detector (Polymer Char, Spain) with flow rate of 0.5 ml/min at 145°C in column zone and

160°C in detector zone. The data was processed by GPC One® software, Polymer Char, Spain.

Crystallization half-time (t_{half} ; min) is the time required to reach 50% of the final crystallinity. It is measured by differential scanning calorimetry (DSC) with a profile heating from 30°C to 200°C at a rate of 50°C/min and holding isothermally at 200°C for 5 min. Then cooling to the specific crystallization temperature (e.g. 136°C) at a rate of 50°C/min and holding for 90°C.

Film properties

Stretchability is observed by appearance when the film is stretched.

Fm/Fy ratio is the value related the thickness variation of the film. Fm is the maximum stretching force at maximum stretching ratio and Fy is a yield of stretching force at initial stretching stage. The force can be monitor from lab scale KARO IV stretching. It can be used to predict the stretchability relatively when the films were stretched at the same condition. The higher value means the better stretchability and better thickness variation should be obtained.

Melting temperature of film (°C) - The peak of melting temperature for all examples was determined using Differential calorimeter (DSC) (Mettler Toledo) according to ASTM D3418 with a profile heating from 30°C to 200°C at a rate of 10 K/min and holding at 200°C for 2 min, then cooling down to 30°C, holding for 2 min and heating to 200°C at a rate of 10 K/min. Under these conditions, the peak Tm was then determined from the melting endotherm.

Specific heat capacity (J/g.K) is measured using Modulated DSC (Mettler Toledo) with a profile heating from 0°C to 250°C at a rate of 1 K/min using Sapphire as a specific heat capacity standard.

Thickness of lamellar crystalline or Lc (μm) is measured using small-angle X-ray scattering (SAXS). SAXS measurement was carried out at the BL1.3 W beamline of the Siam Photon Laboratory, Synchrotron Light Research Institute, Thailand. The SAXS measurement was performed at the sample-to detector distance (SDD) of about 4.5 m, where the scattering vector q , defined as $q = (4\pi/\lambda) \sin(\theta/2)$ (θ : the scattering angle). The lamella thickness was calculated using 1D-electron density correlation function ($K(z)$) following Rungsawang *et al.* Polymer 172 (2019) 41-51.

Porosity is calculated using the following equation:

$$\text{Porosity} = [1 - (\text{Film density after stretching} / \text{Film density before stretching})] \times 100,$$

wherein film density is calculated from the weight and volume or dimensions of the film.

OTR (cc/m². day) was measured at the temperature of 23 °C and 0 %RH using an oxygen transmission rate analyzer (Systech Illinois, 8003) according to ASTM D3985.

WVTR (g/m². day) was measured at the temperature of 37.8 °C and 90 %RH using a water vapour permeation analyzer (PERMATRAN-W®, 3/34) according to ASTM F1249.

Thermal shrinkage (%) is measured according to ASTM D-1204. To 10 centimeters of a film sampling 10 cm x 10 cm, under the condition of 120°C of hot air oven, place 15 min time and cooling by leaving at ambient temperature. Measured machine direction (MD) and transverse direction (TD) size, the two-way size after the thermal contraction and the comparing rate of the two-way size of former state are percent thermal shrinkage.

Tensile modulus (MPa) is measured with a universal testing machine (UTM) (Hounsfield, H5KT) according to ASTM D-882. In the results shown in Table 1 below, MD refers to “longitudinal direction” and TD refers to “transverse direction”.

Tensile strength (MPa) is measured with a UTM machine (Instron model 5565) according to ASTM D-882. In the results shown in Table 1 below, MD refers to “longitudinal direction” and TD refers to “transverse direction”.

Elongation at Break (%) is measured with a UTM machine (Instron model 5565) according to ASTM D-882.

Film thickness (μm) is measured by Vernier digital thickness gauge. The average of film thickness was estimated by measuring the film in the total position of 290 points (MDxTD = 10x29 points).

Haze (%) was measured with Haze meter according to ASTM D-1003 - illuminant C.

Seal strength (kgf) was determined according to the standard ASTM F88-15. BOPP film samples were tested by laminating 20 micron BOPP film with commercial available BOPP film having 18 micron thickness as a middle layer, and using casted with commercial available PP film having 30 micron thickness as a sealing layer. The adhesive for lamination was a mixture of Henkel Liofol UR 3644 and Loctite Liofol LA 6055. The laminated films having 20 micron BOPP film is used for testing of seal strength.

EXAMPLES

EXAMPLES 1 to 4

Homopolypropylene (hPP) having a MWD of 9, a MFR₂ of 4 g/10 min, a tacticity 95% and a M_w of about 370,000 (g/mol) was mixed with various type of β-nucleating agent

and about 500 ppm of Irganox1010, 1000 ppm of Irgafos168, 400 ppm of hydrotalcite 400 ppm at 190-210°C. As shown in Table 1, three different types of beta-nucleating agent were used in the study; calcium tetrahydrophthalate (CT), MPM2000, and N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide (NN).

The resulting pellets were then casted through a film extrusion at a die temperature of 250°C and a chill roll temperature of about 40-60°C. The final cast film had a thickness of 850 µm. The crystallinity and t_{half} of the cast film are shown in Table 1.

The cast film was subsequently biaxially stretched sequentially with a lab-scale stretching machine i.e., Karo IV in MD and subsequently in TD at stretching ratio of 5 and 9, respectively. The MD and TD stretching temperature was 154°C for all PP samples except comparative 4 which is hPP without beta-nucleating agent. Its stretching temperature for MD and TD was 156°C. The test results on the stretched films are shown in Table 1 wherein examples in accordance with the invention are referred to as “Inventive” and comparative examples are referred to as “Comparative”.

At lower chill roll temperature i.e. 42°C, Inventive 1 and Inventive 2 formed a good flatness which was similar to typical hPP material like Comparative 4. Meanwhile, the Comparative 3 was not able to form good flat film i.e., the resultant films were wavy and not good enough for stretching. At higher chill roll temperature i.e. 60°C, Inventive 1 and Inventive 2, as well as Comparative 3 and Comparative 4 were able to form good flat film.

The Comparative 3 could not form good flat cast film because of too fast crystallization rate or too low t_{half} which lead to cannot biaxially orientated stretching or cannot get good thickness variation of the BOPP film. Moreover, considering haze of resulting BOPP film from Karo IV, the haze of Inventive 1 and 2 were lower than 6% as the chill roll temperature at 42°C. The Inventive 1 and 2 were much better stretchability for BOPP application comparing to Comparative 4.

For the heat resistance of BOPP films produced by the lab-scale stretching machine, Inventive 1 and 2 had the higher T_m peak comparing to Comparative 3, and 4. The higher T_m peak of β -nucleated PP (Inventive 1 and 2) lower than neat PP (Comparative 4) due to the β -crystal and transformed β -crystal can enhance the stretchability of polypropylene which can show in higher [Force max (Fm)/Force at yield (Fy)] value from Stress-strain curve that promoted more perfection and higher orientation of α -crystalline structure during stretching for both orientation. However, the lower T_m peak of Comparative 3 due to the poor castability process can affect to the stretchability during bioriented stretching process.

In addition, the specific heat capacity (C_p) in the range of sealing temperature can be indicated the heat resistance of the BOPP films which the lower C_p refer to the faster heat transfer of BOPP films during heat sealing process. The faster heat transfer can prevent the shrinkage of BOPP films which preferable for the high sealing rate. In this invention, Inventive 1, 2 and comparative 3 showed the low value of C_p in the range of 3.20 to 3.36

J/g.K related to the perfection of orientation as explained above. Even the comparative 3 exhibited the high melting peak and low Cp value, however, the yield stress of TDO stretching (~0.6 MPa) had much higher than the β -nucleated PP (~0.1 MPa) conflicting the high production line speed at pilot scale and commercial scale, respectively. For these reasons, this invention clarified that addition of beta nucleating agents with desired formulation can improve both of processability and heat resistance of high crystallinity PP resin capable for using in the BOPP film applications.

Table 1: Properties of Examples

Sample	Inven- tive 1	Inven- tive 2	Compa- rative 3	Compa- rative 4	Compa- rative 5	Inveni ve 6
β -nucleating agent type	Calcium tetrahydrophthalate	MPM2000 (MB)	N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide	No	No	Calcium tetrahydrophthalate
β -nucleating agent content (ppm)	1000	6250 (MB)	1500	0	0	1000
t_{half} @ 136 °C (min)	5.08	2.59	<1	19.69	>20	4.59
MFR ₂ (g/10 min)	4.09	4.34	4.42	3.91	2.05	3.05
Tacticity (%)	95	95	95	95	90	95
MWD	7-9	7-9	7-9	7-9	8-12	7-9
Cast film properties						

Cast film appearance -at CR 42 °C	Smooth /flat sheet	Smooth /flat sheet	Wavy sheet *	Smooth/fl at sheet	Smooth/fl at sheet	Smooth /flat sheet
BOPP film properties						
Stretchbility	Good**	Good**	Not good**	Not good**	Good***	Good** *
Fm/Fy	2.6**	2.4**	N/A	1.5**	1.2***	1.4***
Thickness (µm)	28	28	N/A	26	20.8	20.2
Haze (%)	4.3	5.6	N/A	<2	<2	< 2
Thickness of lamellar crystalline (Lc) (nm)	N/A	N/A	N/A	N/A	19.44	23.42
Tensile Strength (MPa) MD	N/A	N/A	N/A	N/A	152	146
Tensile Strength (MPa) TD	N/A	N/A	N/A	N/A	336	325
Elongation at Break (%) MD	N/A	N/A	N/A	N/A	183	174
Elongation at Break (%) TD	N/A	N/A	N/A	N/A	56	52
E-Modulus (MPa) MD	N/A	N/A	N/A	N/A	2054	2484

E-Modulus (MPa) TD	N/A	N/A	N/A	N/A	4395	4770
Thermal Shrinkage (%) @ 120°C / 15 min – MD	1.0	1.0	N/A	1.5	3.0	1.5
Thermal Shrinkage (%) @ 120°C / 15 min – TD	1.0	1.0	N/A	1.5	2.0	0.75
Tm peak (°C)	170	170	N/A	169	168	171
Cp at 145 °C (J/g.K)	3.36	3.20	N/A	3.35	3.85	3.35
Porosity	0	0	N/A	0	0	0
OTR (cc/m ² .day)	1433	1495	N/A	1326	1510	1647
WVTR (g/m ² · day)	4.7	4.9	N/A	4.4	5.4	5.2

* The cast sheet was wavy and had poor contact with chill roll which affected from crystallization behavior.

** Stretching temperature MD/TD =154/154 °C, Chill roll temperature 42 °C

*** Stretching temperature MD/TD =152/166 °C, Chill roll temperature 42 °C

EXAMPLES 5 to 6

The inventive 6 comprising homopolypropylene having a MFR₂ of 2-3, a MWD of 7-9, a tacticity of 94-96% and a MW of about 390,000 (g/mol) was mixed with Calcium

tetrahydrophthalate as β -nucleating agent and additives, similarly to Inventive 1. For comparison purpose, commodity hPP resin for BOPP production were used as Comparative 5.

The comparative 5 is homopolypropylene having a MFR₂ of 2-3, a MWD of 8-12, a tacticity of 90% and MW of about 460,000 g/mol, commercial BOPP resin from HMC polymer, Thailand.

The characteristics of Inventive 6 and Comparative 5 are summarized in Table 1.

The cast films were subsequently biaxially stretched sequentially with a lab-scale stretching machine i.e., Karo IV in MD and subsequently in TD at stretching ratio of 5 and 9, respectively. The MD and TD stretching temperature was 152°C and 156 °C respectively. The test results on the stretched films are shown in Table 1. The inventive 6 has higher Fm/Fy value than comparative 5. It means that the inventive 6 has better stretchability than comparative 5.

In addition, The Inventive 6 has a higher (peak) melting temperature of BOPP film than commercial BOPP resin and a lower thermal shrinkage. It seems that the higher melting temperature of BOPP film, a lower Cp at an early onset of its melting.

To evaluate heat resistance performance of Inventive 6, the laminate films according to the following film structure with 18 μ m commercial available BOPP (Core layer) and 30 μ m commercial available CPP (sealant side) were tested the sealing performance at 2 bar, 1.0 second at various temperatures.

The sealing strength of inventive 6 was higher than those of Comparative 5 at an early onset of sealing temperature i.e. 145°C (see Figure 1), and (B) Inventive 6 began to thermally shrink at significantly higher temperature than Comparative 5 (see Table 2). These two observation results suggest that Inventive 6 had better heat resistance than comparative 5.

Figure 1 shows that seal strength of the laminated film of the present invention is higher than the seal strength of the comparative examples without nucleating agent.

The Inventive 6 exhibits significantly higher sealing temperature of heat resistance than Comparative 5, see Table 2. The BOPP film made from Inventive 6 can increase packing speed by using higher sealing temperature. Also, the inventive 6 has lower Cp meaning faster heat transfer than Comparative 5. It can be summarized that the Inventive 6 required shorter time to get the same sealing strength. This shows that BOPP film of Inventive 6 can increase the sealing line speed or packing speed during packing process by in form-fill-seal machine.

Table 2: Seal strength and appearance of the tested BOPP film

Sample	Seal strength (kgf) at a temperature, 2 bar, 1.0 Sec				
	135°C	140°C	145°C	150°C	155°C
Comparative 5	0.53	1.29*	2.11*	2.08*	2.16*
Inventive 6	1.24	1.94	2.02	2.18*	2.22*

*Unacceptable appearance due to thermal shrinkage

The features disclosed in the foregoing description and in the dependent claims may, both separately and in any combination thereof, be material for realizing the aspects of the disclosure made in the independent claims, in diverse forms thereof.

CLAIMS

[Claim 1]. A biaxially oriented polypropylene film comprising a composition comprising a polypropylene and a beta-nucleating agent, wherein

- the biaxially oriented polypropylene film has a porosity calculated according to the following formula of less than 0.01, alternatively 0.001, alternatively 0.0001, alternatively 0.00001, alternatively about 0-0.00001,

$$\text{Porosity} = [1 - (d_1/d_0)] \cdot 100$$

wherein d_1 is the density of the biaxially oriented polypropylene film after stretching, and

d_0 is the density of the biaxially oriented polypropylene film before stretching; and

- the composition has a crystallization half-time at 136°C in the range of 1 to 10 min, preferably 2-6 min determined by differential scanning calorimetry under isothermal conditions; an MFR₂ in the range of 2-10 g/10 min, preferably 2-5 g/10 min, determined according to ASTM D-1238-13 at 230 °C 2.16 kg; and
- the polypropylene has a tacticity in the range of 93 to 99 %, preferably 94 to 98 %.

[Claim 2]. The biaxially oriented polypropylene film according to claim 1, wherein the beta-nucleating agent is selected from the group consisting of a metal phthalate, a metal salt, a metal hydrophthalate, or mixtures thereof.

[Claim 3]. The biaxially oriented polypropylene film according to claim 1 or 2, wherein the biaxially oriented polypropylene film has an OTR at 23 °C and 0 %RH of less than 10000 cc/m².day, preferably in the range of 500-5000 cc/m².day, most preferably 1000-3000 cc/m².day, according to ASTM D3985; and/or a WVTR at 38 °C and 90 %RH in the range of 1-20 g/m² · day, preferably 1-10 g/m² · day, according to ASTM F1249.

[Claim 4]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film has a thickness of lamellar crystalline (Lc) of more than 22 nm, alternatively from 22 to 60 nm, preferably from 22 to 40 nm, most preferably 22-30 nm.

[Claim 5]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film comprises the beta-nucleating agent in an amount from 250 to 1,500 ppm by weight,

alternatively 500 to 1,250 ppm by weight, preferably 700 to 1,200 ppm by weight, most preferably 900 to 1,100 ppm by weight, with respect to the total weight of the composition.

[Claim 6]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film further comprises at least one additive selected from an antioxidant, a neutralizer, an inorganic filler, an organic filler or mixtures of two or more thereof.

[Claim 7]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film has a thermal shrinkage by placing a 10x10 cm² sample of the biaxially oriented polypropylene film into hot-air oven at 120°C, 15 min in machine direction (MD) from 0 to 5 %, preferably 0-2% and transverse direction (TD) from 0 to 5 %, preferably 0-2%

[Claim 8]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film has a thickness in the range from 10 to 70 µm, preferably 10 to 50 µm.

[Claim 9]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the composition has a melt flow rate in the range of 2-10 g/10 min, preferably 2 to 5 g/10 min determined according to ASTM D-1238-13 at 230 °C, 2.16 kg.

[Claim 10]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film has a melt temperature (T_m) of film of at least 170°C, preferably 170-175°C.

[Claim 11]. The biaxially oriented polypropylene film according to any of the preceding claims, wherein the biaxially oriented polypropylene film has a haze of less than 7% according to ASTM D-1003 measured on thickness 20 µm, preferably has a haze of 1-6%, most preferably 1-3%.

[Claim 12]. Method for preparing the biaxially oriented polypropylene film according to any of the preceding claims, comprising the steps:

- mixing the polypropylene and the beta-nucleating agent to form pellets;
- extruding the pellets to form a film;
- casting the film with a chill roll temperature in the range of 30-70 °C, preferably 40-60 °C; and
- stretching and annealing the film in machine direction and transverse direction to form the biaxially oriented polypropylene film.

[Claim 13]. A multilayer film comprising the biaxially oriented polypropylene film according to any of the claims 1 to 11.

[Claim 14]. An article comprising the biaxially oriented polypropylene film according to any of the claims 1 to 11.

[Claim 15]. Use of the biaxially oriented polypropylene film according to any of the claims 1 to 11 in a packaging.