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(54) Title: BIAXIALLY ORIENTED LAMINATED FILM FOR WRAPPING FOOD ARTICLES AND METHOD OF MANUFACTURING SAME

(57) Abstract: The present invention relates to a biaxially oriented laminated film for wrapping and a method of manufacturing the same. The inventive biaxially oriented laminated film exhibits excellent performance characteristics in terms of water and gas barrier properties, flex and pinhole resistance, and workability.

BIAXIALLY ORIENTED LAMINATED FILM FOR WRAPPING FOOD ARTICLES AND METHOD OF MANUFACTURING SAME

FIELD OF THE INVENTION

The present invention relates to a biaxially oriented laminated film for wrapping food articles, and a method of manufacturing thereof.

BACKGROUND OF THE INVENTION

A wrapping material for food products is required to have satisfactory gas /water barrier properties and tear-resistance for the preservation of the food during storage and transportation. Accordingly, there have been conducted a number of studies to develop such materials having the above-mentioned properties, as well as transparency and tolerability for microwave use.

For example, Japanese Laid-open Patent Publication No. 1997-289288 discloses a transparent film having excellent gas and water barrier properties, which comprises two layers composed of two or more kinds of inorganic oxides sequentially stacked on one side of a biaxially oriented nylon base film. However, this film tends to undergo undesirable cracking and suffers from processing difficulties due to the tendency of the nylon-6 film to absorb moisture.

Further, Japanese Laid-open Patent Publication Nos. 1996-296138 and 1987-056675 disclose methods for improving gas barrier properties by depositing inorganic oxides on a transparent plastic film. However, they also suffer from the problem of cracking and poor surface characteristics for printing.

Furthermore, Japanese Laid-open Patent Publication No. 2004-351874 discloses a method of manufacturing a transparent barrier film composed essentially of two polyamide (PA) e.g. nylon-6 layers disposed on both sides of a resin layer essentially consisting of an ethylene-vinylalcohol (EVOH) copolymer. Although this method provides improved barrier properties of nylon-6 film, the problem of moisture absorptivity of nylon-6 and ethylene-vinylalcohol copolymer remains unsolved.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a biaxially oriented laminated film for wrapping having excellent performance characteristics in terms of water and gas barrier properties, flex and pinhole resistance, and workability.

In accordance with one aspect of the present invention, there is provided a method of manufacturing a biaxially oriented laminated film, comprising:

(1) melt-extruding a polyamide resin (A) and a polyester resin (B) which satisfying the following equation, to form a two or more layered laminate, and rapidly cooling the laminate to prepare a cast sheet:

$$Tg(A) - 5℃ \leq Tg(B) \leq Tg(A) + 10℃$$

wherein Tg(A) is the glass transition temperature (℃) of the polyamide resin, and Tg(B) is the glass transition temperature (℃) of the polyester resin; and

(2) preheating and biaxially drawing the cast sheet at a temperature which is 5 to 20℃ higher than Tg(A) for 1 to10 seconds.

In accordance with another aspect of the present invention, there is provided a biaxially oriented laminated film manufactured by the method.

In accordance with still another aspect of the present invention, there is provided a wrapping material including the biaxially oriented laminated film.

DETAILED DESCRIPTION OF THE INVENTION

A method of manufacturing a biaxially oriented laminated film according to an embodiment of the present invention includes:

(1) melt-extruding a polyamide resin (A) and a polyester resin (B) which satisfying the following equation, to form a two or more layered laminate, and rapidly cooling the laminate to prepare a cast sheet:

$$Tg(A) - 5℃ \leq Tg(B) \leq Tg(A) + 10℃$$

wherein Tg(A) is the glass transition temperature (℃) of the polyamide resin, and Tg(B) is the glass transition temperature (℃) of the polyester resin; and

(2) preheating and biaxially drawing the cast sheet at a temperature which is 5 to 20℃ higher than Tg(A) for 1 to10 seconds.

In order to manufacture the inventive biaxially oriented laminated film, polyamide resin (A) and polyester resin (B), which satisfies the above equation are melt-extruded using a T-die to form a two or more layered laminate, and then the laminate is rapidly cooled using a cooling roll to prepare a cast sheet.

The polyester resin used in the present invention may be prepared by copolymerizing a diol component with a diacid component. Examples of the diol component include ethylene glycol (EG), 1,3-propanediol (1,3-PDO), neopentyl glycol (NPG), dipropanediol (DPDO), diethylene glycol (DEG), triethylene glycol (TEG), polyethylene glycol (PEG, weight average molecular weight 200 ~ 100,000), 1,4-butanediol (1,4-BDO), 2-methyl-1,2-propanediol (MPDO), 1,4-cyclohexanedimethanol (1,4-CHDM), and propylene glycol. Examples of the

diacid component include terephthalic acid, naphthalene dicarboxylic acid, isophthalic acid, succinic acid, glutaric acid, adipic acid, suberic acid, axelaic acid, sebacic acid, and ester derivatives thereof.

Examples of the polyamide resin used in the present invention include nylon-6, nylon-66, and nylon-MXD6. The barrier properties of the biaxially oriented laminated film can be improved depending on the kind of polyamide resin used.

It is preferred that the polyester resin has a glass transition temperature of which is in the range of -5℃ to +10℃ based on that of the polyamide resin used. For example, as in the case of the present invention where the polyamide resin is used to form an inner layer and the polyester resin is used to form outer layers, when the glass transition temperature of the polyester resin of the outer layer is lower by 5℃ than that of the polyamide resin of the inner layer, there arises the problem that the polyester resin constituting the outer layers undergoes crystallization during the preheating process, and breaks during the drawing process to makes it difficult to form a film. Further, when the glass transition temperature of the polyester resin is higher by 10℃ than that of the polyamide resin, the polyamide resin inner layer undergoes crystallization at the preheating temperature at which the polyester resin is drawn to make it difficult to form a film.

In case a film having a three or more layered laminate structure is manufactured using the method according to the present invention, it is preferred that the outermost layer of the film be made of a polyester resin having a low moisture absorptivity, excellent printability, and workability. In this case, in order to increase the post-workability of the outermost layer after drawing and heat set, inorganic particles may be added to the polyester resin as a slippage promoter (lubricant) before melt-extruding. Examples of such inorganic particles include

silica gel, calcium carbonate, and alumina, having an average particle size of 0.01 to 10 ㎛. The inorganic particles may be added to the polyester resin in an amount appropriate in consideration of the optical characteristics of the film to be manufactured. For example, when a film having excellent transparency is to be manufactured, inorganic particles having a small particle size are mixed with inorganic particles having a large particle size at a proper mixing ratio, and then added to the polyester resin such that the amount of the inorganic particles is 0.04 to 0.07 wt% based on the total amount of polymer. Further, when 0.5 wt% or more of inorganic particles having an average particle size of 5 ㎛ or more are added thereto, a film having low gloss may be obtained. Further, a relatively large amount of titanium dioxide (TiO_2) particles may be added to obtain a white film having improved whiteness, or a relatively large amount of silica gel particles may be added to improve the surface characteristics of the film.

Further, generally, since the adhesivity between a polyamide resin layer and a polyester resin layer is low, an adhesive resin layer may be disposed between the polyamide resin layer and the polyester resin layer in order to improve the adhesion therebetween. That is, the adhesive resin layer is disposed between the polyamide resin layer and polyester resin layer, and then coextruded together with the polyamide resin layer and polyester resin layer to prepare a cast sheet. For example, when the adhesive resin layer (C) is disposed between the polyamide resin layer (A) and polyester resin layer (B) and is then coextruded together with the polyamide resin layer (A) as an inner layer and the polyester resin layers (B) to as outer layers, the prepared cast sheet has a five-layered structure of (B)-(C)-(A)-(C)-(B). It is preferred that the adhesive resin layer be made of a resin which can tightly bind the polyester resin and polyamide resin layers together and maintain transparency after drawing. Bynel (manufactured by DuPont Corp.) may be used

as such an adhesive resin to prepare the adhesive resin layer.

It must be noted that the cast sheet according to the present invention may be prepared through lamination of several nano layers, in which case, the adhesivity between the layers is excellent, and the use of the adhesive resin layer (C) may not be required.

Subsequently, the resulting melt-extruded cast sheet is preheated at a temperature which is 5 to 20℃ higher than the glass transition temperature (Tg) the a polyamide resin for 1 to 10 seconds, and the preheated sheet is subjected to a drawing process. When the preheating time of the cast sheet is less than 1 second, it is difficult to supply a sufficient amount of heat necessary for uniformly drawing the laminate. In contrast, when the preheating time is more than 10 seconds, polymers constituting the respective layers may be crystallized, which makes it difficult to form a film.

Further, when the preheating and drawing temperature of the cast sheet is 5℃ or higher than the Tg of a polyamide resin, the drawing stress of the polyamide resin increases excessively, and to make it difficult to form a film. In contrast, when the cast sheet is preheated and drawn at a temperature 20℃ higher than the Tg of the polyamide resin, the polyester resin of the outer layer of the cast sheet becomes crystallized during the preheating process, which makes it difficult to form a film having uniform thickness.

The drawing process may be performed in both the transverse and longitudinal directions. In the drawing process, the sheet is preferably drawn 1 to 4 times in the transverse direction and the longitudinal direction, respectively.

Additionally, in order to improve the printability, coating adhesion, deposition strength and antistatic properties of the inventive films, one side or both sides of the film may be corona-treated or chemically coated. In case of the

corona treatment, the film may be treated before it is drawn in the transverse and longitudinal directions, or may be treated before it is drawn in the transverse and longitudinal directions and then wound. Further, a finished film may be treated using an off-line coating method. For the chemical coating treatment, the film may be in-line coated before it is drawn in the transverse and longitudinal directions, or the finished film may be coated off-line.

Further, in order to improve the gas barrier properties of the film according to the present invention, a predetermined amount of nano-clay particles having a plate(flake)-like structure may be added to at least one of the polyamide resin and polyester resin. In this case, the nano-clay particles may be added at the time of the preparation of the polyamide resin and polyester resin or before the melt-extruding of the laminate. Examples of the nano-clay particles having flake-type structure include biotite, lepidolite, kaolinite, halloysite, montmorillonite, margarite, talc, chlorite, and the like.

Furthermore, in order to improve the gas barrier properties of the film according to the present invention, one side or both sides of the laminate and the monoaxially or biaxially oriented film may be coated with nano-clay, SiOx, or Al_2Ox (wherein, x is 1, 2 or 3) particles.

The present invention comprises the biaxially oriented laminated film for wrapping manufacture by the method.

Further, the present invention comprises a wrapping material manufactured by combining the biaxially oriented laminated film with a substrate using a thermal adhesive resin layer on at least one side thereof, and it may be used in the post-treatment of forming the biaxially oriented laminated film into an envelope shaped film through a thermal adhesion method. The thermal adhesive resin layer may be made of linear low-density polyethylene (LLDPE) or cast polypropylene (CPP).

The following Examples are now given for the purpose of illustration only, and are not intended to limit the scope of the invention.

Example 1

A laminate was prepared using a Nylon 6 (glass transition temperature(Tg) = 45 ℃) film (A) as an inner layer, two polytrimethylene terephthalate (Tg = 42℃) films (B) as outer layers, and two Bynel resin films (C)(DuPont Corp.) as adhesive layers disposed between the inner and the outer layers. The laminate thus obtained was coextruded with a T-die to prepare a cast sheet having a five-layered structure of (B)-(C)-(A)-(C)-(B).

The cast sheet thus obtained was drawn at a draw ratio of 2.8 in the longitudinal direction using a drawing roll kept at 55℃ and a cooling roll kept at 25℃. The resulting sheet was preheated to 50℃ for 3 seconds, and drawn at a draw ratio of 3.2 in the transverse direction at 60℃ using a tenter. The resulting oriented film was heat set at 190℃, cooled, and subjected to 10% relaxation at 150℃, to obtain a biaxially oriented film having a thickness of 15 ㎛.

Comparative Example 1

The procedure of Example 1 was repeated except for preheating the sheet to 50℃ for 12 seconds before drawing in the transverse direction to obtain a film.

Comparative Example 2

The procedure of Example 1 was repeated except for preheating and drawing in transverse direction at 65℃ to obtain a film.

Example 2

The procedure of Example 1 was repeated except for using adipic acid-copolymerized polytrimethylene terephthalate (Tg = 38℃) ,produced by copolymerizing a diacid component comprising 5 mol% of adipic acid and 95 mol% of terephthalic acid with 1,3-propanediol in place of Nylon 6, to obtain a biaxially oriented film having a thickness of 15 ㎛.

Example 3

The procedure of Example 1 was repeated except for using polytetramethylene terephthalate (Tg = about 38℃) in place of polytrimethylene terephthalate, to obtain a biaxially oriented film having a thickness of 15 ㎛.

Example 4

Nylon-MXD6 (Tg = about 81℃)(A) and polytrimethylene naphthalate (Tg = 78℃)(B) were coextruded using the procedure of Example 1 to prepare a cast sheet

The cast sheet thus obtained was drawn at a draw ratio of 3 in the longitudinal directions using a drawing roll kept at 85℃ and a cooling roll kept at 25℃. The resulting sheet was preheated to 90℃ for 5 seconds, and drawn at a draw ratio of 3.5 in the transverse direction at 95℃ using a tenter. Then, the resulting oriented film was heat set at 210℃, cooled, and subjected to 3.5 % relaxation at 150℃, to obtain a biaxially oriented film having a thickness of 15 ㎛.

Example 5

The procedure of Example 1 was repeated except for using nylon-6

nanocomposite resin (M1030DH, manufactured by Unitika Ltd.) containing plate-like nano-clay particles in place of Nylon 6, to obtain a biaxially oriented film having a thickness of 15 ㎛.

Comparative Example 3

The physical properties of a commercially available polyethylene terephthalate film having a thickness of 15 ㎛ were measured and they were compared with those of the films manufactured in Examples of the present invention.

Comparative Example 4

The physical properties of a commercially available nylon-6 film having a thickness of 15 ㎛ were measured and they were compared with those of the films manufactured in Examples of the present invention.

Experimental Example

The physical properties of the films manufactured in Examples and Comparative Examples were evaluated as follow, and the results are shown in Table 1.

(1) Oxygen transmission rate (OTR)

A sample film was cut to a size of 15 cm × 15 cm based on the JIS L 1096 standards. The cut film was mounted on a gas transmission rate (GTR) tester manufactured by Toyoseki Ltd., and the amount of oxygen passed through the cut film during a predetermined time was measured to determine the oxygen

transmission rate (unit: $cc/m^2/atm/day$) of the cut film, using a computer program.

(2) Water vapor transmission rate (WVTR)

The water vapor transmission rate (unit: $g/m^2/day$) of a sample film was measured based on ASMT F 372 standards using a moisture meter (PERMATRAN-W (model name), manufactured by Mocon Ltd.).

(3) Glass transition temperature (Tg)

Each of the resins used in the Examples and Comparative Examples was melt-extruded under prescribed conditions through a T die, and rapidly cooled on a cooling roll maintained at 30℃, to prepare a cast sheet having a thickness of 150 to 200 ㎛. The glass transition temperatures (Tg, ℃) of the sheet was measured under a nitrogen atmosphere at a heating rate of 10℃/min using a differential scanning calorimeter (DSC) manufactured by Perkin-Elmer Corp.

(4) Flex and pinhole resistance

A sample film was subjected to a rotational stress test using Gelbo Flex (Gelbo Inc., USA) at an angle of 450 degree for 500 cycles. Next, the sample film was placed flat on a white paper, whereon an a general solvent nitroglycerin (NC) ink was applied with a doctor blade. The number of ink dots appeared on the white paper was measured as the pin-hole number. An average value derived from 3 repeated tests was used to represent each sample.

Table 1

	polyester resin		polyamide resin		transverse drawing process			film physical properties			evaluation
	used	Tg (℃)	used	Tg (℃)	preheating temperature (℃)	preheating time (second)	drawing temperature (℃)	OTR (cc/m^2/atm/day)	WVTR (g/m^2/day)	flex & pinhole resistance	
Exp. 1	PTT	42	PA-6	45	50	3	60	31	32	0	
Exp. 2	AA(5)-Co-PTT	38	PA-6	45	50	3	60	31	28	0	
Exp. 3	PBT	38	PA-6	45	50	3	60	34	29	0	
Exp. 4	PTN	78	PA-MXD6	81	90	5	95	3	35	0	
Exp. 5	PTT	42	PA-Compo site	45	50	3	60	4	5	0	
Comp. Exp. 1	PTT	42	PA-6	45	50	12	60	-	-	-	Unevenly drawn
Comp. Exp. 2	PTT	42	PA-6	45	65	3	65	-	-	-	Unevenly drawn
Comp. Exp. 3	PET	76	-		-	-	-	120	40	crack	only PET film
Comp. Exp. 4	-		PA-6	45	-	-	-	40	180	0	only PA-6 film

PTT: polytrimethylene terephthalate

PA-6: nylon-6

PBT: polytetramethylene terephthalate

PTN: polytrimethylene naphthalate

PET: polyethylene terephthalate

AA(5)-co-PTT: PTT copolymerized with 5 mol% of adipic acid

PA-MXD6: nylon-MXD6 (prepared by the condensation and polymerization of methaxylene diamine and adipic acid)

PA-Composite: nylon-6 resin (nylon-6 nanocomposite) containing plate-like nano-clay particles

OTR: oxygen transmission rate

WVTR: water vapor transmission rate

As described above, the biaxially oriented laminated film for wrapping according to the present invention is superior to the conventional films in terms of water and gas barrier properties, toughness such as flex and pinhole resistance, and workability such as printability and bondability, and controlling the water and gas barrier properties.

While the invention has been shown and described with respect to the preferred embodiments, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the following claims.

WHAT IS CLAIMED IS:

1. A method of manufacturing a biaxially oriented laminated film, comprising:

(1) melt-extruding a polyamide resin (A) and a polyester resin (B) which satisfying the following equation, to form a two or more layered laminate, and rapidly cooling the laminate to prepare a cast sheet:

$Tg(A) - 5℃ \leq Tg(B) \leq Tg(A) + 10℃$

wherein Tg(A) is the glass transition temperature (℃) of the polyamide resin, and Tg(B) is the glass transition temperature (℃) of the polyester resin; and

(2) preheating and biaxially drawing the cast sheet at a temperature which is 5 to 20℃ higher than Tg(A) for 1 to10 seconds.

2. The method of manufacturing a biaxially oriented laminated film of claim 1, wherein the polyamide resin is selected from the group consisting of nylon-6, nylon-66 and nylon-MXD6.

3. The method of manufacturing a biaxially oriented laminated film of claim 1, wherein the polyester resin is prepared by copolymerizing a diol component selected from the group consisting of ethylene glycol, 1,3-propanediol, neopentyl glycol, dipropanediol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,4-butanediol, 2-methyl-1,2-propanediol, 1,4-cyclohexanedimethanol, and propylene glycol with a diacid component selected from the group consisting of terephthalic acid, naphthalene dicarboxylic acid, isophthalic acid, succinic acid, glutaric acid, adipic acid, suberic acid, axelaic acid, sebacic acid, and ester derivatives thereof.

4. The method of manufacturing a biaxially oriented laminated film of claim 1, wherein at least one of the polyamide resin and polyester resin contains nano-clay particles.

5. The method of manufacturing a biaxially oriented laminated film of claim 1, further comprising:

coating the laminate or the biaxially oriented film with a nano-clay, SiOx, or Al_2Ox (wherein, x is 1, 2 or 3) particles on at least one side thereof.

6. The method of manufacturing a biaxially oriented laminated film of claim 4 or 5, wherein the nano-clay particles are selected from the group consisting of particles of biotite, lepidolite, kaolinite, halloysite, montmorillonite, margarite, talc, and chlorite.

7. A biaxially oriented laminated film for wrapping, which is manufactured by the method of claim 1.

8. A wrapping material manufactured by combining the biaxially oriented laminated film of claim 7 with a substrate using a thermal adhesive resin layer.

9. The wrapping material of claim 8, wherein the thermal adhesive resin layer is made of a linear low-density polyethylene (LLDPE) or a cast polypropylene (CPP).