EUROPEAN PATENT SPECIFICATION

THERMOPLASTIC FILM STRUCTURES WITH A LOW MELTING POINT OUTER LAYER

Designated Contracting States: DE ES FR GB IT

Priority: 03.12.2002 US 308702

Date of publication of application: 31.08.2005 Bulletin 2005/35

Proprietor: ExxonMobil Oil Corporation
Irving, TX 75039-2298 (US)

Inventors:
- LU, Pang-Chia
  Pittsford, NY 14534 (US)
- PEET, Robert, G.
  Pittsford, NY 14534 (US)
- AMBROISE, Benoit
  B-6720 Hachy (BE)
- VAN DEN BOSSCHE, Linda
  B-2070 Zijndrecht (BE)
- VANDERHEYDEN, Nancy
  B-3201 Langdrop (BE)
- BOSCH, François
  B-6762 Saint-Mard (BE)
- MORIAU, Jacques
  F-54269 Grand-Failly (FR)
- MENDES, Lindsay
  Rochester, NY 14610 (US)
- WRIGHT, Syd, R.
  Pittsford, NY 14534 (US)
- TROCH, Geneviève et al
  ExxonMobil Chemical Europe Inc.
  P.O. Box 105
  1830 Machelen (BE)

Representative: Troch, Geneviève et al
ExxonMobil Chemical Europe Inc.
P.O. Box 105
1830 Machelen (BE)

References cited:
EP-A-0 668 157
EP-A-0 695 630
WO-A-98/37140

Report of one person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
DESCRIPTION

BACKGROUND OF THE INVENTION

[0001] The invention relates to multilayer thermoplastic film structures comprising at least one low melting point outer layer, and methods of manufacturing multilayer thermoplastic film structures comprising at least one low melting point outer layer.

[0002] Thermoplastic film structures are used in a wide variety of applications. Of the many different types of thermoplastic film structures, so-called oriented polypropylene (OPP) film structures, including biaxially oriented polypropylene (BOPP) film structures, which comprise at least one polypropylene-containing layer, are a very popular choice. OPP film structures possess excellent optical and mechanical characteristics, in addition to excellent barrier characteristics, e.g., moisture-barrier characteristics. OPP film structures, however, are not ideal in every respect.

[0003] For example, packaging applications, lamination applications, and metal adhesion applications are just some examples of the wide variety of applications in which thermoplastic film structures may be employed. For many packaging applications, the film structure must exhibit good sealing characteristics. For lamination applications, the film structure must achieve strong lamination bonds with the substrate to which it is being laminated. The metal layer of a metallized film structure must strongly adhere to the metallized layer of the film structure.

[0004] The extension of unmodified OPP film structures into packaging, lamination, and metal adhesion applications has been somewhat hampered by the difficulties associated with providing an OPP film structure that possesses: adequate heat-seal characteristics over a wide temperature range for packaging applications; adequate lamination bond strengths for lamination applications; or adequate metal adhesion for metallized film structures.

[0005] One solution has been to apply a coating having excellent heat-sealing, laminating, and/or metallizing characteristics onto an outer surface of an OPP film structure. An example of such a coating is a coating comprising a low melting point polymer may be applied onto an outer surface of a polypropylene-containing film structure via an in-line extrusion coating process. In an in-line extrusion coating process, which may be used in conjunction with a sequential tenter frame orients, a coating comprising a low melting point polymer is applied onto an outer surface of a polypropylene-containing film structure after the film structure has been formed and then oriented in the machine-direction, but before the film structure has been oriented in the transverse direction.

[0006] According to one approach, a coating comprising a low melting point polymer may be applied onto an outer surface of a polypropylene-containing film structure via an in-line extrusion coating process. In an in-line extrusion coating process, which may be used in conjunction with a sequential tenter frame orients, a coating comprising a low melting point polymer is applied onto an outer surface of a polypropylene-containing film structure after the film structure has been formed and then oriented in the machine-direction, but before the film structure has been oriented in the transverse direction.

[0007] According to a different approach, a coating comprising a low melting point polymer may be applied onto an outer surface of a polypropylene-containing film structure via an in-line extrusion coating process. In an in-line extrusion coating process, which may be used in conjunction with a sequential tenter frame orients, a coating comprising a low melting point polymer is applied onto an outer surface of a polypropylene-containing film structure after the film structure has been formed and then oriented in the machine-direction, but before the film structure has been oriented in the transverse direction.

[0008] Regardless of whether an in-line or off-line coating technique is employed, the bond adhesion obtained between the polypropylene-containing layer and certain low melting point polymers that may serve as the coating, such as an ethylene-vinyl acetate (EVA) copolymer, may be less than adequate.

[0009] One method to improve bond strength is to corona-treat the substrate before extrusion coating the, e.g., EVA copolymer, thereon, or to ozone-treat the, e.g., EVA copolymer, before it contacts the substrate. Bond strength, however, is not always sufficient with either of these methods, and, furthermore, odor and corrosiveness are issues with ozone.

[0010] A reliable method to achieve high bond adhesion is to apply a primer layer between the substrate and the low melting point coating. Examples of suitable primers include imine-type, water-based primers and polyurethane-type primers. The application of a primer, however, makes the process (i) more complicated, because the primer solution has to be prepared and diluted, and (ii) more expensive, because the drying time for the primer limits the coating speed.

[0011] It would be advantageous to be able to provide, without the need for primer, a film structure exhibiting good bond adhesion between an extrusion-coated, low melting point polymer, such as an EVA copolymer coating, and the substrate to which the coating is applied.

[0012] In addition, it must be noted that via off-line coating, a film structure is provided wherein the low melting point coating has not at all been oriented. Via in-line extrusion coating, a film structure is provided wherein the low melting point coating has been oriented in only one direction, i.e., the transverse direction.

[0013] WO 98/37140 discloses an oriented multilayer film comprising at least one outer layer comprising an ethylene copolymer having a density of 0.9 to 0.935 g/cm³ contacted with a polypropylene core layer made by coextrusion of said layers and subsequent orientation done by using the sequential tenter frame method. However attempts to manufacture a coextruded, biaxially oriented film structure comprising at least a polypropylene-containing base layer and an outer layer comprising a low melting point polymer have been hampered by the machine-direction orientation step in conventional methods of manufacturing biaxially oriented film structures. Specifically, the machine-direction orientation step may require machine-direction orientation (MDO) roll temperatures above about 220 °F (104 °C) in order to properly
stretch the base layer. Therefore, a low melting point polymer may not be coextruded and machine-direction oriented by such a method because a low melting point polymer that contacts MDO rolls at such temperatures tends to disadvantageously stick to the MDO rolls. Other complications arising from contacting a low melting point polymer outer layer with relatively high temperature MDO rolls include residue build-up, optical defects, and the potential for forming holes in the film sheets that leads to breaks and production interruption.

It would therefore be advantageous to be able to coextrude and biaxially orient a film structure comprising at least a polypropylene-containing base layer and an outer layer comprising a low melting point polymer.

SUMMARY OF THE INVENTION

There is provided a coextruded, biaxially orientated film structure comprising at least a base layer comprising a thermoplastic polymer and a first outer layer comprising a low melting point thermoplastic polymer selected from the group consisting of ethylene plasomers, ethylene-vinyl acetate (EVA) copolymers, ethylene-acrylic acid (EVA) copolymers or terpolymers, and blends thereof, the coextruded, biaxially oriented film structure being prepared by coextruding melts corresponding to each individual layers of the film structure through a die and thereafter simultaneously biaxially stretching the coextruded film sheet on a line using linear motors that directly propel pairs of tenter clips synchronously.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic polymers used in the base layer is an isotactic propylene homopolymer having an isotacticity of from 89 to 99% (as measured by 13C NMR spectroscopy using meso pentads), a melting point of from 311°F (155 °C) to 329 °F (165°C), and a melt flow rate of from 0.5 to 15 g/10 minutes (as measured according to ASTM D1238). The isotactic propylene polymer may be produced by using Ziegler-Natta or metallocene catalysts. Metalloocene-catalyzed isotactic polypropylenes made developmentally or commercially are EOD 96-21 and EOD 97-09, from Fina Oil and Chemical Co., EXPP-129, from ExxonMobil Chemical Co., and Novalen M, from BASF GmbH, among others.

In certain embodiments there may be added to the base layer from 0.0002 to 8 wt%, based on the weight of polypropylene, more preferably from 0.005 to 2 wt%, e.g., from 0.01 to 2 wt%, of a beta nucleator. Any type of beta nucleator may be employed, including two-component beta nucleators. Alternatively, a base layer of a film structure according to the present invention may not comprise any beta-nucleator.

If it is desired to produce an opaque film structure, a cavitating agent(s) may be dispersed with the polymeric matrix of the base layer. A suitable cavitating agent(s) includes any organic or inorganic material that is incompatible with (the term "incompatible" is used in the sense that the materials are two distinct phases), and has a higher melting point than, the film-forming polymer of the base layer, at least at the orientation temperature. For example, the cavitating agent(s) may be any of those described in U.S. Patent Nos. 4,377,616 and 4,632,869. Specific examples of the cavitating agent(s) include polybutylene terephthalate (PBT), nylon, an acrylic resin, an ethylene-norborne copolymer, solid or hollow preformed glass spheres, metal beads or spheres, ceramic spheres, calcium carbonate, and combinations thereof. When the base layer comprising a cavitating agent(s) is subjected to uniaxial or biaxial orientation, a cavity forms, providing a film having an opaque appearance.

The particle size of the cavitating agent(s) may be, for example, from 0.1 micron to 10 microns, more preferably from 0.2 micron to 2 microns. The cavitating agent(s) may be of any desired shape. For example, the cavitating agent(s) may be substantially spherical. The cavitating agent(s) may be present in the base layer in an amount of less than 30 wt%, for example from 2 wt% to 20 wt%, e.g., from 5 wt% to 10 wt%, based on the total weight of the base layer.

The cavitating agent(s) may be dispersed within the polymeric matrix of the base layer by blending the cavitating agent(s) and the film-forming polymer that provides the polymeric matrix at a temperature above the melting point of the film-forming polymer. This blending may take place in an extruder, such as a corotating, intermeshing twin screw extruder.

To preserve the structural integrity of the base layer, a thin layer of the film-forming polymer of the base layer, without the cavitating agent(s), may be coextruded on one or both sides of the film-forming polymer of the base layer. In this case, the total of the cavitating agent(s)-containing layer and the non-cavitating agent(s)-containing layer(s) may be considered the overall base layer of the film.

The base layer may also comprise an opacifying agent(s). Examples of the opacifying agent(s) include iron oxide, carbon black, titanium dioxide, talc, and combinations thereof. The opacifying agent(s) may be present in the base layer in an amount of from 1 to 15 wt%, for example from 1 to 8 wt%, e.g., from 2 to 4 wt%, based on the total weight of the base layer. Aluminum is another example of an opacifying agent that may be used in the base layer of the present film structure. Aluminum may be included in the base layer as an opacifying agent in an amount of from 0.1 to 1.0 wt%, e.g., from 0.25 to 0.85 wt%, based on the total weight of the base layer.

The base layer may further comprise one or more hydrocarbon resins. The hydrocarbon resin(s) may be present in the base layer in a total amount of from 1 wt% to 15 wt%, for example from 1 wt% to 12 wt%, e.g., from 2 wt% to 6 wt%, based upon the total weight of the base layer.

The hydrocarbon resin(s) may be a low molecular weight hydrocarbon which is compatible with the film-
forming polymer of the base layer. The hydrocarbon resin(s) may, optionally, be hydrogenated. The hydrocarbon resin(s) may have a number average molecular weight of less than 5,000, for example less than 2,000, e.g. from 500 to 1,000. The resin(s) may be natural or synthetic and may have a softening point in the range of from 140 °F to 356 °F (60 °C to 180 °C). A specific example of a hydrocarbon resin that may be contained in the present base layer is any of the hydrocarbon resins disclosed in U.S. Patent No. 5,667,902 to Brew, et al. Specific examples include, but are not limited to, petroleum resins, terpene resins, styrene resins, and cyclopentadiene resins. Examples of commercially available hydrogenated resins include PICCOCYTE, REGALREZ, and REGALITE, each of which are available from Hercules Corp., ESCOREZ, available from ExxonMobil Chemical Co., and ARKON, available from Arakawa Chemical Co.

A saturated alicyclic resin is an additional example of a hydrocarbon resin that may be included in the base layer of the present film structure. Saturated alicyclic resins have a softening point in the range of from 185 °F to 284 °F (85 °C to 140 °C), for example from 212 °F to 284 °F (100 °C to 140 °C), as measured by the ring and ball technique. An example of a commercially available saturated alicyclic resin is ARKON-P, available from Arakawa Forest Chemical Industries, Ltd. Of Japan.

The base layer of the film structure is of sufficient thickness to provide bulk properties, such as barrier or stiffness that are desired for product protection and good performance on packaging equipment. In preferred embodiments, the thickness of the base layer ranges from 50% to 99% of the entire thickness of the film structure.

The film structure comprises at least a first outer layer. The first outer layer comprises a low melting point thermoplastic polymer having a melting point of not more than 230 °F (110 °C), e.g., from 113 °F to 230 °F (45 °C to 110 °C). For more amorphous polymers that may not have a well-defined crystalline melting point, suitable low melting point polymers include those that have a Vicat softening point of not more than 85 °C (185 °F).

The first outer layer comprises a low melting point thermoplastic polymer selected from the group consisting of ethylene plastomers, ethylene-vinyl acetate (EVA) copolymers, ethylene-acrylic acid (EAA) copolymers or terpolymers and blends thereof. In general, ethylene plastomers are film-forming plastomers that are produced via well known single-site (including metallocene) catalyst technology, which permits very precise control of (i) the comonomer incorporated into an ethylene polymer and (ii) the molecular weight distribution. Ethylene plastomers may be copolymers of ethylene with higher α-olefins having from 3 to 10 carbon atoms, such as, for example, 1-butene, 1-hexene and 1-octene. Preferred ethylene plastomers for use as the film-forming plastomer of the first outer layer have a density range of from 0.865 to 0.889 g/cm³ and a peak melting point range of from 120 °F to 185 °F (from 49 °C to 85 °C). Ethylene plastomers are commercially available from ExxonMobil Chemical Company, under the trademark EXACT. Ethylene plastomers are also commercially available from Dow Plastics, Dow U.S.A., Midland, Mich., under the trademark ENGAGE, e.g., ENGAGE EG8100 (an ethylene/1-octene copolymer), or AFFINITY.

Ethylene-vinyl acetate copolymers are film-forming copolymers having from 1 wt% to 45 wt% of vinyl acetate comonomer content, and the remainder of ethylene. A particularly preferred range of the vinyl acetate comonomer content is from 5 wt% up to 30 wt%, e.g., from 6 wt% up to 21 wt%. Preferably, the ethylene-vinyl acetate copolymer has a melt index of from 0.5 to 28 g/10 min (ASTM D1238; 190 °C/2.16 kg) and a peak melting point range of from 113 °F to 212 °F (from 45 °C to 100 °C). Ethylene-vinyl acetate copolymers are commercially available from, for example, ExxonMobils Chemical Company under the trade name ESCORENE ULTRA.

Ethylene acrylic acid (EAA) copolymers and terpolymers are film-forming copolymers and terpolymers that comprise (i) polyethylene, (ii) acrylic acid, or mixtures thereof with, methacyric acid, and/or (iii) alkyl acrylate, alkyl methacrylate, or mixtures thereof, e.g., ethylene-butyl acrylate copolymer, ethylene-ethyl acrylate copolymer, etc. For example, an ethylene acid terpolymer resin composition may comprise: (i) from 0.5 wt% to 12 wt% of acrylic acid, or mixtures thereof with methacrylic acid; (ii) up to 20 wt% of alkyl acrylate, alkyl methacrylate, or mixtures thereof, preferably from 6 wt% to 20 wt% of alkyl acrylate, alkyl methacrylate, or mixtures thereof; and (iii) the remainder of polyethylene. Preferred EAA copolymers and terpolymers for use as the film-forming polymers of the first outer layer have a melting point range of from 140 °F to 212 °F (from 60 °C to 100 °C). Examples of EAA copolymers and terpolymers include ESCOR 5000 (melt index=8 g/10 minutes (ASTM D1238); density=0.931 g/cm³; 6 wt% acrylyc acid), ESCOR 5050 (melt index=8 g/10 minutes (ASTM D1238); density=0.936 g/cm³; 9 wt% acrylic acid), and ESCOR 5100 (melt index=8 g/10 minutes (ASTM D1238); density=0.940 g/cm³; 11 wt% acrylic acid), which are commercially available ethylene-acrylic acid copolymers, and ESCOR AT-310 (melt index=6 g/10 minutes (ASTM D1238); density=0.943 g/cm³), and ESCOR AT-320 (melt index=5 g/10 minutes (ASTM D1238); density=0.953 g/cm³), which are commercially available acid terpolymers. ESCOR resins are commercially available from ExxonMobil Chemical Company.

The film structure may comprise the first outer layer applied directly on one side of the base layer, or the film structure may comprise one or more intermediate, or tie, layers between the base layer and the first outer layer.

The film structure may additionally comprise one or more layers on the side of the base layer opposite the side of the first outer layer. For example, the film structure may comprise a second outer layer applied di-
directly on the side of the base layer opposite the first outer layer, or the film structure may comprise one or more intermediate, or tie, layers between the base layer and second outer layer.

[0034] The second outer layer, if present, comprises a polymeric matrix comprising a film-forming polymer.

[0035] In one embodiment of the invention, the film-forming polymer of the second outer layer is the same as the film-forming polymer of the first outer layer, i.e., the second outer layer is also a low melting point polymer.

[0036] For other embodiments of the invention, the film-forming polymer used to form the polymeric matrix of the second outer layer may be chosen from a list of materials including, but not limited to, polyolefins, such as polypropylene, syndiotactic polypropylene, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ethylene copolymers, such as ethylene-vinyl acetate and ethylene-vinyl alcohol copolymers, nylons, polymers grafted with functional groups (including, but not limited to, maleic and fumaric anhydride), blends of these, etc. MDPE has a density in the range of from 0.925 g/cm³ to 0.940 g/cm³.

[0037] For certain embodiments, it may be desirable for the second outer layer to be a heat-seal layer. For example, it may be desirable for the film-forming polymer of the second outer layer to comprise polyolefinic copolymers, terpolymers, or blends thereof.

[0038] Suitable heat-seal copolymers include block or random copolymers of ethylene and propylene, butylene and propylene, and ethylene and butylene. A preferred copolymer is an ethylene-propylene (EP) random copolymer generally containing from 2 to 8 wt% ethylene, specifically from 3 to 7 wt% ethylene, the balance being made up of propylene. The copolymer may have a melt index at 446 °F (230 °C) generally ranging from 2 to 15 g/10 min (ASTM D1238), and preferably from 3 to 8 g/10 min. The crystalline melting point is usually from 257 °F to 302 °F (from 125 °C to 150 °C) and the number average molecular weight range is from 25,000 to 100,000. The density will usually range from 0.89 to 0.92 g/cm³. An example of a commercially available copolymer that may be used as the second outer layer is 7880 PP, available from CHISSO.

[0039] Suitable heat-seal terpolymers include ethylene-propylene-butene-1 terpolymers. A preferred terpolymer is an ethylene-propylene-butene-1 (EPB) terpolymer obtained from the random inter-polymerization of from 1 to 8 weight percent ethylene, preferably from 3 to 7 weight percent ethylene with from 1 to 10 weight percent butene-1, preferably from 2 to 8 weight percent butene-1 with propylene representing the balance. The foregoing EPB terpolymers may be characterized by a melt index at 446 °F (230 °C) of from 2 to 16 g/10 min (ASTM D1238), and advantageously from 3 to 7 g/10 min, a crystalline melting point of from 212 °F to 284 °F (from 100 °C to 140 °C), an average molecular weight of from 25,000 to 100,000 and a density within the range of from 0.89 to 0.92 g/cm³. An example of a commercially available terpolymer that may be used as the second outer layer is XPM 7510, available from CHISSO.

[0040] If a blend of EPB terpolymer and EP copolymer is used as the second outer layer, the blend may contain from 10 to 90 weight percent EPB terpolymer and preferably from 40 to 60 weight percent EPB terpolymer, the balance being made up of EP copolymer.

[0041] According to additional embodiments of the invention, the outer surface of the second outer layer has a glossy appearance. This may be accomplished by several manners known in the art.

[0042] For example, a polymer that possesses high gloss optical characteristics when formed into a film may be specifically selected as the film-forming polymer of the second outer layer. Examples of such polymers are well known in the art, and include polyolefins, such as homopolymers of propylene or ethylene. Blends of film-forming polymers for the second outer layer may also be employed, provided that a combination of incompatible polymers is not employed. The presence of two or more incompatible polymers may negatively affect the gloss optical characteristics.

[0043] To further ensure that the film-forming polymer selected for the second outer layer will provide a glossy appearance, the level of gloss-impairing additives, especially certain slip additives, such as fatty amides, silicone oil, and certain antistatic agents, added to the second outer layer may be controlled, or if necessary, kept at nil. In addition, or alternatively, to further enhance the glossy appearance of the film-forming polymer selected for the second outer layer, a particular coating, such as a high-gloss polyurethane coating, may be applied to the outer surface of the second outer layer.

[0044] According to still further embodiments of the invention, the outer surface of the second outer layer has a matte appearance. This may be accomplished by several manners known in the art. For example, a blend of two or more incompatible polymers may be employed as the film-forming polymers of the second outer layer, or a coating that imparts a haze may be applied to the outer surface of the second outer layer. U.S. Patent No. 6,087,015 to Cretekos, et al. provides some specific example of matte surface layers.

[0045] The intermediate layer(s) that is optionally provided between the base layer and the first outer layer and/or between the base layer and the second outer layer comprises a polymeric matrix comprising a film-forming polymer. Suitable film-forming polymers for forming the polymeric matrix of the intermediate layer(s) include, but are not limited to, polyolefins, such as polypropylene, syndiotactic polypolypropylene, polypropylene copolymers, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ethylene copolymers, nylons, polymers grafted with functional groups or blends of these.

[0046] Although the thickness of the film structure, and
the thicknesses of the individual layers of the film structure, are not critical, in certain embodiments, the film structure has a total thickness ranging from 0.2 mil to 5 mils (5 μm to 130 μm) preferably from 0.4 mil to 2.5 mils (10 μm to 65 μm). The thickness of the base layer preferably ranges from 50% to 99%, the thickness of each intermediate layer, if any, preferably ranges from 0% to 25%, and the thickness of each outer layer(s) preferably ranges from 1% to 15%, wherein, for each case, the example range is based on the entire thickness of the film structure. In certain embodiments, the thickness of the coated layer may be from 30 to 70%.

In order to modify or enhance certain properties of the film structure for specific end-uses, it is possible for one or more of the layers to contain appropriate additives in effective amounts. Preferred additives include, but are not limited to anti-blocks, anti-static agents, coefficient of friction (COF) modifiers, processing aids, colorants, clarifiers, ionomers and other additives known to those skilled in the art.

Thus, a film structure according to the present invention comprises at least a base layer comprising a thermoplastic polymer and at least a first outer layer comprising a low melting point polymer.

In contrast to related prior art film structures, however, each of the individual layers of a film structure prepared according to preferred embodiments of the present invention, including the base layer and first outer layer, are coextruded and biaxially oriented, for example, from 1.5 to 8 times in the machine direction and from 2 to 12 times in the transverse direction, e.g., from 4 to 6 times in the machine direction and from 8 to 10 times in the transverse direction.

According to the invention, melts corresponding to each of the individual layers of the film structure, including the first outer layer, are prepared and coextruded through a die, e.g., a flat-film die or slot die, quenched, and then the film sheet comprising the coextruded layers is subjected to a simultaneous biaxial orientation process that does not employ machine-direction orientation (MDO) rolls. The result is a coextruded, biaxially oriented film structure wherein the low melting point polymer co-extruded as the first outer layer of the film structure does not disadvantageously stick to any MDO rolls.

Specifically, simultaneous biaxial orientation proceeds on a line that utilizes linear motors to directly propel opposed pairs of tenter clips synchronously. A film sheet comprising each of the coextruded layers of the film structure to be produced may be primarily oriented by synchronously accelerating along a diverging path a multitude of directly opposed pairs of tenter clips holding the film sheet, thus achieving simultaneous biaxial orientation and providing the biaxially oriented film structure. In addition, secondary machine-direction orientation on the same tenter can be effected along a parallel, or substantially parallel, path subsequent to the diverging path by simultaneously accelerating the directly opposed pairs of tenter clips along some portion of the parallel path.

The use of linear motors to directly propel tenter clips to effect simultaneous biaxial stretching is further disclosed in U.S. Pat. No. 4,853,602 to Hommes, et al.

As would be readily understood by one of ordinary skill in the art, the simultaneous stretching works equally well, whether the film structure to be produced is limited to a base layer and first outer layer, or whether the film structure to be produced further comprises any of the additional layers disclosed herein, including one or more intermediate layers and/or a second outer layer.

One or both of the outer surfaces of the coextruded, biaxially oriented film structure, e.g., one or both of the first and second outer layers, or one or both of the first outer layer and the base layer where the film structure does not include a second outer layer, may be surface-treated. The surface treatment can be carried out by any method known in the art, including, but not limited to, corona discharge treatment, flame treatment, or plasma treatment. Although any of these techniques are effectively employed to surface-treat the outer layer(s), a particularly desirable method of treatment is the so-called corona treatment method, which comprises exposing the film surface to a high voltage corona discharge while passing the film between a pair of spaced electrodes. The surface of the outer layer(s) may be treated to a surface tension level of at least 35 dynes/cm (35 mN/m) e.g. from 38 to 55 dynes/cm (38 to 55 mN/m), in accordance with ASTM Standard D2578-84.

In addition, the outer surface of the side of the coextruded, biaxially oriented film structure opposite the first outer layer, e.g., the outer surface of the second outer layer, or the outer surface of the base layer where the film structure does not include a second outer layer, may have a coating applied thereto via, e.g., an off-line coating process. An appropriate coating includes, but is not limited to, an acrylic coating, such as those described in U.S. Patent Nos. 3,753,769 and 4,865,908, an acrylonitrile coating, a polyvinylidene chloride (PVdC) coating, such as those described in U.S. Patent Nos. 4,214,039, 4,447,494, 4,961,992, 5,019,447, and 5,057,177; a polyvinyl alcohol (PVOH) coating, a urethane coating, an epoxy coating, and blends thereof.

Examples of commercially available PVOH materials include VINOL 125, 99.3+ % super hydrolyzed polyvinyl alcohol and VINOL 325, 98% hydrolyzed polyvinyl alcohol, each of which may be obtained from Air Products, Inc. For additional examples of PVOH coatings that may be used to coat the second outer layer, see, for example, U.S. Patent Nos. 4,927,689, 5,230,963, and 5,547,764.

The coating may be applied in an amount such that there will be deposited upon drying a smooth, evenly distributed layer, generally on the order of from 0.01 to 1 mil (0.25 to 25 μm) thickness. Generally, the coating comprises 1 to 25 wt%, preferably 7 to 15 wt% of the entire coated film structure. The coating on the film structure is subsequently dried by hot air, radiant heat or by
any other convenient means.

[0058] Prior to the application of the coating, the outer surface of the side of the coextruded, biaxially oriented film structure opposite the first outer layer may be primed with a primer material. An appropriate primer material includes, but is not limited to, a poly(ethyleneimine) primer and an epoxy primer.

[0059] The outer surface of the side of the coextruded, biaxially oriented film structure opposite the first outer layer, e.g., the outer surface of the second outer layer, the outer surface of the base layer where the film structure does not include a second outer layer, or the outer surface of the coating where a coating has been applied to that side of the film structure, may be metallized. Application of a metal coating layer may be accomplished by vacuum deposition, or any other metallization technique, such as electroplating or sputtering. The metal of the metal coating layer may be aluminum, or any other metal capable of being vacuum deposited, electroplated, or sputtered, such as, for example, gold, zinc, copper, or silver. The thickness of the deposited metal coating may be from 5 to 200 nanometers (nm), for example, from 10 to 100 nm, e.g. from 30 to 80 nm.

[0060] The provision of a first outer layer of a low melting point polymer, e.g., plastomer or EVA, lends the film structure superior functionality. For example, for packaging applications, the first outer layer provides the film structure with excellent sealing characteristics. For lamination applications, the first outer layer allows the film structure to achieve strong lamination bonds with the substrate to which it is being laminated. In addition, the first outer layer allows the metal layer of a metallized film structure to strongly adhere to the film structure.

[0061] A film structure according to the invention may be used for low temperature seal, high speed packaging use, for low temperature over-lamination to paper or other plastic substrates, document lamination, "plastification," or for digital printing with selected surface chemistry.

[0062] In a particular application, the first outer layer of a film structure according to the invention is laminated onto a substrate. The substrate may be glass, plastic, ceramic, metal, textiles, electronics or wood. For example, the substrate may be another polymer film or laminate, a cellulosic web(s), e.g., numerous varieties of paper, such as corrugated paperboard, craft paper, glassine, and cartonboard, nonwoven tissue, e.g., spunbonded polyolefin fiber or melt-blown microfibers.

[0063] In a preferred embodiment, a film structure according to the invention is laminated via the first outer layer as a protective film for an identification card or display system used for advertising, including signs, posters or pictures.

[0064] While the lamination of a film structure to a substrate may employ a suitable adhesive, e.g., a hot melt adhesive, such as blends of HEVA, waxes and resins or a water-based adhesive, such as polyvinylidene chloride latex, between the first outer layer and substrate, film structures prepared according to the present invention may be advantageously laminated by heat lamination.

[0065] Heat lamination, which uses heat and pressure to apply a lamination film onto a substrate, improves the durability of the substrate without the need for more expensive water-based lamination or environmentally unfriendly solvent-based lamination. Commercial heat laminators used for the lamination of film structures to paper substrates, such as cards, can be standalone machines in which a printed card is fed into the laminator where an overlay film is applied to the card. In this case, a film structure according to the present invention may advantageously be employed as the overlay film. Alternatively, the laminator may be integrated into a printer.

[0066] For other applications, the first outer layer of the film structure is metallized. Application of a metal coating layer to the first outer layer may be accomplished by vacuum deposition, or any other metallization technique, such as electroplating or sputtering. The metal of the metal coating layer may be aluminum, or any other metal capable of being vacuum deposited, electroplated, or sputtered, such as, for example, gold, zinc, copper, or silver. The thickness of the deposited metal coating may be from 5 to 200 nanometers (nm), for example, from 10 to 100 nm, e.g. from 30 to 80 nm.

Claims

1. A coextruded, biaxially oriented film structure comprising a base layer comprising a thermoplastic polymer and a first outer layer comprising a thermoplastic polymer that has a melting point of not more than 230 °F (110°C) characterised in that:

   • the thermoplastic polymer of the base layer is an isotactic propylene homopolymer having and isotacticity of from 89 to 99%, a melting point of from 311°F (155°C) to 329°F (165°C) and a melt flow rate of from 0.5 to 15 g/10 minutes measured according to ASTM D1238, and
   • the thermoplastic polymer of the first outer layer is selected from the group consisting of ethylene plastomers, ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers or terpolymers and blends thereof,

   the film structure being prepared by coextruding melts corresponding to each individual layer of the film structure through a die to form a coextruded film sheet and simultaneously biaxially orienting the coextruded film sheet on a line using linear motors that directly propel opposed pairs of tenter clips synchronously.

2. The film structure of claim 1, further comprising an intermediate layer on one side of the base layer and the first outer layer is on a side of the intermediate
3. The film structure of claim 2, wherein the intermediate layer comprises an ethylene polymer.

4. The film structure of claim 1, further comprising a second outer layer disposed on a side of the base layer opposite the first outer layer.

5. The film structure according to any of the preceding claims, wherein the film structure has been oriented from 1.5 to 8 times in the machine direction and from 2 to 12 times in the transverse direction.

6. The film structure of any of the preceding claims, wherein at least one outer surface of the film structure has been surface-treated by one of corona discharge treatment, flame treatment and plasma treatment.

7. The film structure of any of the preceding claims, further comprising a coating applied on an outer surface of one side of the film structure opposite the first outer layer.

8. The film structure of any of the preceding claims, further comprising a metallized layer applied to an outer surface of a side of the film structure opposite the first outer layer.

9. The film structure of any of the preceding claims, wherein the first outer layer is heat-sealed to a substrate.

10. The film structure of any of the preceding claims, further comprising a substrate laminated to the first outer layer of the film structure.

Patentansprüche

1. Koextrudierte biaxial orientierte Folienstruktur, die eine Basisschicht, die ein thermoplastisches Polymer enthält, und eine erste äußere Schicht umfasst, und eine erste äußere Schicht umfasst, die ein thermoplastisches Polymer enthält, das einen Schmelzpunkt von nicht mehr als 230°F (110°C) aufweist, dadurch gekennzeichnet, dass

   • das thermoplastische Polymer der Basisschicht isotaktisches Propylenhomopolymer mit einer Isotaktizität von 89 bis 99%, einem Schmelzpunkt von 311°F (155°C) bis 329°F (165°C) und einem gemäß ASTM D1238 gemessenen Schmelzflußindex (melt flow rate) von 0,5 bis 15 g/10 Minuten ist und
   • das thermoplastische Polymer der ersten äußeren Schicht ausgewählt ist aus der Gruppe bestehend aus Ethylenplastomeren, Ethylen-
Revendications

1. Structure de film orienté biaxialement, coextrudé, comprenant un couche de base comprenant un polymère thermoplastique et une première couche extérieure comprenant un polymère thermoplastique qui possède un point de fusion ne dépassant pas 230°F (110°C), caractérisée en ce qui :

• le polymère thermoplastique de la couche de base est un homopolymère de propylène isotactique ayant une isotacticité de 89 à 99%, un point de fusion de 311°F (155°C) à 329°F (165°C) et un indice de fluidité à chaud de 0,5 à 15 g/10 minutes, mesuré selon ASTM D1238 ;

et

• le polymère thermoplastique de la première couche extérieure est choisi dans le groupe constitué par les plastomères d’éthylène, les copolymères éthylène-acétate de vinyle, les copolymères éthylène-acide acrylique et leurs mélanges,

la structure de film étant préparée par coextrusion de coulées correspondant à chaque couche individuelle de la structure de film à travers une filière pour former une feuille de film coextrudé et simultanément par orientation biaxiale de la feuille de film coextrudé sur une chaîne en utilisant des moteurs linéaires qui entraînent directement des paires opposées de pinces de rame de façon synchrone.

2. Structure de film selon la revendication 1, comprenant en outre une couche intermédiaire d’un côté de la couche de base et la première couche extérieure est du côté de la couche intermédiaire opposé à la couche de base.

3. Structure de film selon la revendication 2, dans laquelle la couche intermédiaire comprend un polymère d’éthylène.

4. Structure de film selon la revendication 1, comprenant en outre une deuxième couche extérieure placée du côté de la couche de base opposé à la première couche extérieure.

5. Structure de film selon l’une quelconque des revendications précédentes, dans laquelle la structure de film a été orientée de 1,5 à 8 fois dans le sens machine et de 2 à 12 fois dans le sens travers.

6. Structure de film selon l’une quelconque des revendications précédentes, dans laquelle au moins une surface extérieure de la structure de film a été soumise à un traitement de surface consistant en un traitement de décharge corona, un traitement à la flamme ou un traitement en plasma.

7. Structure de film selon l’une quelconque des revendications précédentes, comprenant en outre un revêtement appliqué sur une surface extérieure du côté de la structure de film opposé à la première couche extérieure.

8. Structure de film selon l’une quelconque des revendications précédentes, comprenant en outre une couche métallisée appliquée sur une surface extérieure située du côté de la structure de film opposé à la première couche extérieure.


10. Structure de film selon l’une quelconque des revendications précédentes, comprenant en outre un substrat stratifié sur la première couche extérieure de la structure de film.
REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader’s convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 9837140 A [0013]
- US 4377616 A [0018]
- US 4632869 A [0018]
- US 5667502 A, Brew [0024]
- US 6087015 A, Cretekos [0044]
- US 4853602 A, Hommes [0052]
- US 3753769 A [0055]
- US 4865908 A [0055]
- US 4214039 A [0055]
- US 4447494 A [0055]
- US 4961992 A [0055]
- US 5019447 A [0055]
- US 5057177 A [0055]
- US 4927689 A [0056]
- US 5230963 A [0056]
- US 5547764 A [0056]