(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 August 2019 (15.08.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/156733 A1

(51) International Patent Classification:
C09D 5/24 (2006.01) *G06F 1/16* (2006.01)
G02B 5/22 (2006.01)

(21) International Application Number:
PCT/US2018/063695

(22) International Filing Date:
03 December 2018 (03.12.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/628,629 09 February 2018 (09.02.2018) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

WO 2019/156733 A1

(54) Title: POLYETHYLENE FILM COMPOSITIONS, LAMINATES, AND METHODS FOR MAKING THE SAME

(57) Abstract: Disclosed are transparent films having a core comprising at least 50 wt.% high-density polyethylene and, optionally, 50 wt.% or less of linear low-density polyethylene. Further, the transparent films may have a printable skin layer adjacent to a first side of the core, wherein the printable skin layer may comprise, consists essentially of or consists of linear low-density polyethylene or ethylene-propylene copolymer. Further, the transparent films may have a skin layer adjacent to a second side of the core, wherein the skin layer may comprise, consists essentially of or consists of linear low-density polyethylene or ethylene-propylene copolymer. Further still, the transparent films may be oriented in at least one direction and have a directional modulus of at least 1200 MPa. Such transparent films may be laminated to a laminating substrate, such as a biaxially oriented polyethylene single or multilayer film, to produce a laminated film with remarkable sealing and integrity.

POLYETHYLENE FILM COMPOSITIONS, LAMINATES, AND METHODS FOR MAKING THE SAME

REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Patent Cooperation Treaty application, which claims priority to United States provisional patent application serial number 62/628,629 filed on 9 February 2018 that is hereby incorporated by reference in its entirety.

FIELD

[0002] This disclosure relates to compositions, structures, and methods for polyethylene films that include both barrier protection and enhanced sealing properties in packaging, wrapping and labeling applications.

BACKGROUND

[0003] Polyethylene films are broadly used as sealants in packaging. Un-oriented films generally have mediocre physical properties and need to be combined to other webs such as paper, PET, BOPP, and so forth in order to provide mechanical strength, or such as metallized PET, metallized BOPP, Nylon or aluminum foil in order to provide barrier protection. Although orienting often improves strength, it also negatively affects sealing properties, which is not good for packaging. Moreover, traditional cast or blown polyethylene sealant films are typically not metallized since metal adhesion does not adhere well enough to maintain integrity when laminated to a stiff web.

[0004] What is needed are new multilayer films that have barrier protection with enhanced sealing properties and integrity for packages. Furthermore, what is needed are new

multilayer films that withstand metallization and provide good metal adhesion and metallized barrier properties.

SUMMARY

[0005] Disclosed are transparent films having a core comprising at least 50 wt.% high-density polyethylene and, optionally, 50 wt.% or less of linear low-density polyethylene. Further, the transparent films may have a printable skin layer adjacent to a first side of the core, wherein the printable skin layer may comprise, consists essentially of or consists of linear low-density polyethylene or ethylene-propylene copolymer. Further, the transparent films may have a skin layer adjacent to a second side of the core, wherein the skin layer may comprise, consists essentially of or consists of linear low-density polyethylene or ethylene-propylene copolymer. Further still, the transparent films may be oriented in at least one direction and have a directional modulus of at least 1200 MPa. Such transparent films may be laminated to a laminating substrate, such as a biaxially oriented polyethylene single or multilayer film, to produce a laminated film with remarkable sealing and integrity.

BACKGROUND

[0006] Below, directional terms, such as “above,” “below,” “upper,” “lower,” “front,” “back,” “top,” “bottom,” etc., are used for convenience in referring to the accompanying drawings. In general, “above,” “upper,” “upward,” “top,” and similar terms refer to a direction away the earth’s surface, and “below,” “lower,” “downward,” “bottom,” and similar terms refer to a direction toward the earth’s surface, but is meant for illustrative purposes only, and the terms are not meant to limit the disclosure.

[0007] Various specific embodiments, versions and examples are described now, including exemplary embodiments and definitions that are adopted herein for purposes of understanding. While the following detailed description gives specific preferred

embodiments, those skilled in the art will appreciate that these embodiments are exemplary only, and that the disclosure can be practiced in other ways. For purposes of determining infringement, the scope of the invention will refer to the any claims, including their equivalents, and elements or limitations that are equivalent to those that are recited.

[0008] Generally, disclosed are optionally oriented (*i.e.*, monoaxially and/or biaxially), multilayer, polyethylene ("PE") films that are optionally laminated to PE substrate, metallized or not, so as to create a mono-material laminate in some embodiments, which may, for instance, permit easy recycling, and/or in some embodiments improve stiffness as compared to incumbent films and laminates thereof.

[0009] As used herein, "polymer" may be used to refer to homopolymers, copolymers, interpolymers, terpolymers, etc. Likewise, a "copolymer" may refer to a polymer comprising two monomers or to a polymer comprising three or more monomers.

[0010] As used herein, "intermediate" is defined as the position of one layer of a multilayered film, wherein said layer lies between two other identified layers. In some embodiments, the intermediate layer may be in direct contact with either or both of the two identified layers. In other embodiments, additional layers may also be present between the intermediate layer and either or both of the two identified layers.

[0011] As used herein, "elastomer" is defined as a propylene-based or ethylene-based copolymer that can be extended or stretched with force to at least 100% of its original length, and upon removal of the force, rapidly (*e.g.*, within 5 seconds) returns to its original dimensions.

[0012] As used herein, "plastomer" is defined as a propylene-based or ethylene-based copolymer having a density in the range of 0.850 g/cm^3 to 0.920 g/cm^3 and a DSC melting point of at least 40 °C.

[0013] As used herein, "substantially free" is defined to mean that the referenced film layer is largely, but not wholly, absent a particular component. In some embodiments, small amounts of the component may be present within the referenced layer as a result of standard manufacturing methods, including recycling of film scraps and edge trim during processing.

[0014] By "consist essentially of," what is meant, for example, is that a particular film layer does not have any more than 1 wt % or 2 wt % or 3 wt % or 4 wt % or 5 wt % of other polymers in the bulk material constituting the film layer's composition, but "consist essentially of" does not exclude the possibility that the particular film layer also has additives, such as anti-slip agents, anti-blocking agents, anti-oxidants, pigments, whitening agents, cavitation agents, etc. regardless of what polymers or other materials make up the additive(s).

Core Layer

[0015] As is known to those skilled in the art, the core layer of a multilayered film is most commonly the thickest layer and provides the foundation of the multilayered structure. In some embodiments, the core layer comprises, consists essentially of, or consists of biaxially oriented polyethylene ("BOPE"), such as a high-density polyethylene film ("HDPE") and/or other PE's having a density greater than 0.94 g/cm^3. In alternative embodiments, the core layer may also include other polymers, including, for instance, biaxially oriented polypropylene ("BOPP"), biaxially oriented polyester ("BOPET"), biaxially oriented polylactic acid ("BOPLA"), and combinations thereof. In still alternate embodiments the core layer may also contain lesser amounts of additional polymer(s) selected from the group consisting of ethylene polymer, ethylene-propylene copolymers, ethylene-propylene-butene terpolymers, elastomers, plastomers, different types of metallocene-LLDPEs (m-LLDPEs), and combinations thereof.

[0016] The core layer may further include a hydrocarbon resin. Hydrocarbon resins may serve to enhance or modify the flexural modulus, improve processability, or improve the barrier properties of the film. The resin may be a low molecular weight hydrocarbon that is compatible with the core polymer. Optionally, the resin may be hydrogenated. The resin may have a number average molecular weight less than 5000, preferably less than 2000, most preferably in the range of from 500 to 1000. The resin can be natural or synthetic and may have a softening point in the range of from 60 °C to 180 °C.

[0017] Suitable hydrocarbon resins include, but are not limited to petroleum resins, terpene resins, styrene resins, and cyclopentadiene resins. In some embodiments, the hydrocarbon resin is selected from the group consisting of aliphatic hydrocarbon resins, hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, hydrogenated cycloaliphatic/aromatic hydrocarbon resins, hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosins and rosin esters, hydrogenated rosins and rosin esters, and combinations thereof.

[0018] The amount of such hydrocarbon resins, either alone or in combination, in the core layer is preferably less than 20 wt %, more preferably in the range of from 1 wt % to 5 wt %, based on the total weight of the core layer.

[0019] The core layer may further comprise one or more additives such as opacifying agents, pigments, colorants, cavitating agents, slip agents, antioxidants, anti-fog agents, anti-static agents, fillers, moisture barrier additives, gas barrier additives, and combinations thereof, as discussed in further detail below. A suitable anti-static agent is ARMOSTAT™ 475 (commercially available from Akzo Nobel of Chicago, Ill.).

[0020] Cavitating agents may be present in the core layer in an amount less than 30 wt %, preferably less than 20 wt %, most preferably in the range of from 2 wt % to 10 wt %, based on the total weight of the core layer.

[0021] Preferably, the total amount of additives in the core layer comprises up to about 20 wt % of the core layer, but some embodiments may comprise additives in the core layer in an amount up to about 30 wt % of the core layer.

[0022] The core layer preferably has a thickness in the range of from about 5 μm to 100 μm, more preferably from about 5 μm to 50 μm, most preferably from 5μm to 25 μm.

Tie Layer(s)

[0023] Tie layer(s) of a multilayered film is typically used to connect two other layers of the multilayered film structure, *e.g.*, a core layer and a sealant layer, and is positioned intermediate these other layers. The tie layer(s) may have the same or a different composition as compared to the core layer.

[0024] In some embodiments, the tie layer is in direct contact with the surface of the core layer. In other embodiments, another layer or layers may be intermediate the core layer and the tie layer. The tie layer may comprise one or more polymers. In addition, the polymers may include C_2 polymers, maleic-anhydride-modified polyethylene polymers, C_3 polymers, C_2C_3 random copolymers, $C_2C_3C_4$ random terpolymers, heterophasic random copolymers, C_4 homopolymers, C_4 copolymers, metallocene polymers, propylene-based or ethylene-based elastomers and/or plastomers, ethyl-methyl acrylate (EMA) polymers, ethylene-vinyl acetate (EVA) polymers, polar copolymers, and combinations thereof. For example, one polymer may be a grade of VISTAMAXX™ polymer (commercially available from ExxonMobil Chemical Company of Baytown, Tex.), such as VM6100 and VM3000 grades. Alternatively, suitable polymers may include VERSIFY™ polymer (commercially available from The Dow Chemical Company of Midland, Mich.), Basell CATALLOY™ resins such as ADFLEX™

T100F, SOFTELL™ Q020F, CLYRELL™ SM1340 (commercially available from Basell Polyolefins of The Netherlands), PB (propylene-butene-1) random copolymers, such as Basell PB 8340 (commercially available from Basell Polyolefins of The Netherlands), Borealis BORSOFT™ SD233CF, (commercially available from Borealis of Denmark), EXCEED™ 1012CA and 1018CA metallocene polyethylenes, EXACT™ 5361, 4049, 5371, 8201, 4150, 3132 polyethylene plastomers, EMCC 3022.32 low density polyethylene (LDPE) (commercially available from ExxonMobil Chemical Company of Baytown, Tex.).

[0025] In some embodiments, the tie layer may further comprise one or more additives such as opacifying agents, pigments, colorants, cavitating agents, slip agents, antioxidants, anti-fog agents, anti-static agents, anti-block agents, fillers, moisture barrier additives, gas barrier additives, and combinations thereof, as discussed in further detail below.

[0026] The thickness of the tie layer is typically in the range of from about 0.50 to 25 μm, preferably from about 0.50 μm to 12 μm, more preferably from about 0.50 μm to 6 μm, and most preferably from about 2.5 μm to 5 μm. However, in some thinner films, the tie layer thickness may be from about 0.5 μm to 4 μm, or from about 0.5 μm to 2 μm, or from about 0.5 μm to 1.5 μm.

Skin Layer(s), Including Metallizable Skin Layers and Printable Layers

[0027] In some embodiments, the skin layer comprises at least one polymer selected from the group comprising, consisting essentially of, and/or consisting of polyethylene copolymers or terpolymers, which may be grafted or copolymerized. In some embodiments, the polyethylene(s) may comprise an acid-containing portion, which may be acrylic-acid based, methacrylic-acid based, another organic acid, or combinations thereof. The acid-containing portion of the acid-containing polymer may be from 4 wt% through 20 wt%, or 6 wt% through 16 wt%, or 8 wt% through 12 wt%. As examples, Exxon Mobil Escor EAA resins or Dupont Nucrel EAA resins or Dow Primacor EAA resins might be used. For metallizing or

barrier properties, the acid-modified skin layer may contain LLDPE or ethylene vinyl alcohol based polymer(s) ("EVOH"), a suitable EVOH copolymer is EVAL™ G176B or XEP 1300 (commercially available from Kuraray Company Ltd. of Japan).

[0028] The skin layer may also comprise processing aid additives, such as anti-block agents, anti-static agents, slip agents and combinations thereof, as discussed in further detail below.

[0029] The thickness of the skin layer depends upon the intended function of the skin layer, but is typically in the range of from about 0.20 μm through 3.5 μm, or from 0.30 μm through 2 μm, or in many embodiments, from 0.50 μm through 1.0 μm. In thin film embodiments, the skin layer thickness may range from about 0.20 μm through 1.5 μm, or 0.50 μm through 1.0 μm.

Additives

[0030] Additives present in the film's layer(s) may include, but are not limited to opacifying agents, pigments, colorants, cavitating agents, slip agents, antioxidants, anti-fog agents, anti-static agents, anti-block agents, fillers, moisture barrier additives, gas barrier additives, gas scavengers, and combinations thereof. Such additives may be used in effective amounts, which vary depending upon the property required.

[0031] Examples of suitable opacifying agents, pigments or colorants are iron oxide, carbon black, aluminum, titanium dioxide (TiO_2), calcium carbonate ($CaCO_3$), and combinations thereof.

[0032] Cavitating or void-initiating additives may include any suitable organic or inorganic material that is incompatible with the polymer material(s) of the layer(s) to which it is added, at the temperature of biaxial orientation, in order to create an opaque film. Examples of suitable void-initiating particles are PBT, nylon, solid or hollow pre-formed glass spheres, metal beads or spheres, ceramic spheres, calcium carbonate, talc, chalk, or

combinations thereof. The average diameter of the void-initiating particles typically may be from about 0.1 to 10 μm.

[0033] Slip agents may include higher aliphatic acid amides, higher aliphatic acid esters, waxes, silicone oils, and metal soaps. Such slip agents may be used in amounts ranging from 0.1 wt % to 2 wt % based on the total weight of the layer to which it is added. An example of a slip additive that may be useful is Erucamide®.

[0034] Non-migratory slip agents, used in one or more skin layers of the multilayered films, may include polymethyl methacrylate (PMMA). The non-migratory slip agent may have a mean particle size in the range of from about 0.5 μm to 8 μm, or 1 μm to 5 μm, or 2 μm to 4 μm, depending upon layer thickness and desired slip properties. Alternatively, the size of the particles in the non-migratory slip agent, such as PMMA, may be greater than 20% of the thickness of the skin layer containing the slip agent, or greater than 40% of the thickness of the skin layer, or greater than 50% of the thickness of the skin layer. The size of the particles of such non-migratory slip agent may also be at least 10% greater than the thickness of the skin layer, or at least 20% greater than the thickness of the skin layer, or at least 40% greater than the thickness of the skin layer. Generally spherical, particulate non-migratory slip agents are contemplated, including PMMA resins, such as EPOSTAR™ (commercially available from Nippon Shokubai Co., Ltd. of Japan). Other commercial sources of suitable materials are also known to exist. Non-migratory means that these particulates do not generally change location throughout the layers of the film in the manner of the migratory slip agents. A conventional polydialkyl siloxane, such as silicone oil or gum additive having a viscosity of 10,000 to 2,000,000 centistokes is also contemplated.

[0035] Suitable anti-oxidants may include phenolic anti-oxidants, such as IRGANOX® 1010 (commercially available from Ciba-Geigy Company of Switzerland). Such an anti-

oxidant is generally used in amounts ranging from 0.1 wt % to 2 wt %, based on the total weight of the layer(s) to which it is added.

[0036] Anti-static agents may include alkali metal sulfonates, polyether-modified polydiorganosiloxanes, polyalkylphenylsiloxanes, and tertiary amines. Such anti-static agents may be used in amounts ranging from about 0.05 wt % to 3 wt %, based upon the total weight of the layer(s).

[0037] Examples of suitable anti-blocking agents may include silica-based products such as SYLOBLOC® 44 (commercially available from Grace Davison Products of Colombia, Md.), PMMA particles such as EPOSTAR™ (commercially available from Nippon Shokubai Co., Ltd. of Japan), or polysiloxanes such as TOSPEARL™ (commercially available from GE Bayer Silicones of Wilton, Conn.). Such an anti-blocking agent comprises an effective amount up to about 3000 ppm of the weight of the layer(s) to which it is added.

[0038] Useful fillers may include finely divided inorganic solid materials such as silica, fumed silica, diatomaceous earth, calcium carbonate, calcium silicate, aluminum silicate, kaolin, talc, bentonite, clay and pulp.

[0039] Optionally, nonionic or anionic wax emulsions can be included in the coating(s), *i.e.*, sealant layer(s), to improve blocking resistance and /or lower the coefficient of friction. For example, an emulsion of Michem Lube 215, Michem Lube 160 may be included in the sealant layer(s). Any conventional wax, such as, but not limited to Carnauba™ wax (commercially available from Michelman Corporation of Cincinnati, Ohio) that is useful in thermoplastic films is contemplated.

Metallization

[0040] The outer surface (*i.e.*, side facing away from the core) of a skin layer and/or laminating substrate may undergo metallization after optionally being treated. Metallization may be carried out through conventional methods, such as vacuum metallization by

deposition of a metal layer such as aluminum, copper, silver, chromium, or mixtures thereof. Following metallization, a coating may be applied to the outer metallized layer "outside" or "inside" the vacuum chamber to result in the following structure: metallized layer/sealant layer/core/sealant layer/metallized layer. In an additional embodiment, a primer may be applied on the metal surface(s) followed by top coating(s).

[0041] In certain embodiments, the metal for metallization is metal oxide, any other inorganic materials, or organically modified inorganic materials, which are capable of being vacuum deposited, electroplated or sputtered, such as, for example, SiOx, AlOx, SnOx, ZnOx, IrOx, wherein x = 1 or 2, organically modified ceramics "ormocer", etc. The thickness of the deposited layer(s) is typically in the range from 100 to 5,000 Angstrom or preferably from 300 to 3000 Angstrom.

Surface Treatment

[0042] One or both of the outer surfaces of the multilayered films may be surface-treated to increase the surface energy to render the film receptive to metallization, coatings, printing inks, adhesives, and/or lamination. The surface treatment can be carried out according to one of the methods known in the art including corona discharge, flame, plasma, chemical treatment, or treatment by means of a polarized flame.

Priming

[0043] An intermediate primer coating may be applied to multilayered films. In this case, the film may be first treated by one of the foregoing methods to provide increased active adhesive sites thereon and to the thus-treated film surface there may be subsequently applied a continuous coating of a primer material. Such primer materials are well known in the art and include, for example, epoxy, poly(ethylene imine) (PEI), and polyurethane materials. U.S. Pat. No. 3,753,769, U.S. Pat. No. 4,058,645 and U.S. Pat. No. 4,439,493, each incorporated herein by reference, discloses the use and application of such primers. The

primer provides an overall adhesively active surface for thorough and secure bonding with the subsequently applied coating composition and can be applied to the film by conventional solution coating means, for example, by roller application.

Orienting

[0044] The films herein are also characterized in certain embodiments as being biaxially oriented. The films can be made by any suitable technique known in the art, such as a tentered or blown process, LISIM™, and others. Further, the working conditions, temperature settings, lines speeds, etc. will vary depending on the type and the size of the equipment used. Nonetheless, described generally here is one method of making the films described throughout this specification. In a particular embodiment, the films are formed and biaxially oriented using the tentered method. In the tentered process, line speeds of greater than 100 m/min to 400 m/min or more, and outputs of greater than 2000 kg/h to 4000 kg/h or more are achievable. In the tenter process, sheets/films of the various materials are melt blended and coextruded, such as through a 3, 4, 5, 7-layer die head, into the desired film structure. Extruders ranging in diameters from 100 mm to 300 or 400 mm, and length to diameter ratios ranging from 10/1 to 50/1 can be used to melt blend the molten layer materials, the melt streams then metered to the die having a die gap(s) within the range of from 0.5 or 1 to an upper limit of 3 or 4 or 5 or 6 mm. The extruded film is then cooled using air, water, or both. Typically, a single, large diameter roll partially submerged in a water bath, or two large chill rolls set at 20 or 30 to 40 or 50 or 60 or 70 °C are suitable cooling means. As the film is extruded, an air knife and edge pinning are used to provide intimate contact between the melt and chill roll.

[0045] Downstream of the first cooling step in this embodiment of the tentered process, the unoriented film is reheated to a temperature of from 80 to 100 or 120 or 150 °C, in one embodiment by any suitable means such as heated S-wrap rolls, and then passed between

closely spaced differential speed rolls to achieve machine direction orientation. It is understood by those skilled in the art that this temperature range can vary depending upon the equipment, and in particular, upon the identity and composition of the components making up the film. Ideally, the temperature will be below that which will melt the film, but high enough to facilitate the machine direction orientation process. Such temperatures referred to herein refer to the film temperature itself. The film temperature can be measured by using, for example, infrared spectroscopy, the source aimed at the film as it is being processed; those skilled in the art will understand that for transparent films, measuring the actual film temperature will not be as precise. The heating means for the film line may be set at any appropriate level of heating, depending upon the instrument, to achieve the stated film temperatures.

[0046] The lengthened and thinned film is passed to the tenter section of the line for TD orientation. At this point, the edges of the sheet are grasped by mechanical clips on continuous chains and pulled into a long, precisely controlled hot air oven for a pre-heating step. The film temperatures range from 100 or 110 to 150 or 170 or 180 °C in the pre-heating step. Again, the temperature will be below that which will melt the film, but high enough to facilitate the step of transverse direction orientation. Next, the edges of the sheet are grasped by mechanical clips on continuous chains and pulled into a long, precisely controlled hot air oven for transverse stretching. As the tenter chains diverge a desired amount to stretch the film in the transverse direction, the process temperature is lowered by at least 2 °C but typically no more than 20 °C relative to the pre-heat temperature to maintain the film temperature so that it will not melt the film. After stretching to achieve transverse orientation in the film, the film is annealed at a temperature below the melting point, and the film is then cooled from 5 to 10 or 15 or 20 or 30 or 40 °C below the stretching temperature, and the clips

are released prior to edge trim, optional coronal, printing and/or other treatment can then take place, followed by winding.

[0047] Thus, TD orientation is achieved by the steps of pre-heating the film having been machine oriented, followed by stretching and annealing it at a temperature below the melt point of the film, and then followed by a cooling step at yet a lower temperature. In one embodiment, the films described herein are formed by imparting a transverse orientation by a process of first pre-heating the film, followed by a decrease in the temperature of the process within the range of from 2 or 3 to 5 to 10 or 15 or 20 °C relative to the pre-heating temperature while performing transverse orientation of the film, followed by a lowering of the temperature within the range of from 5 °C to 10 or 15 or 20 or 30 or 40 °C relative to the melt point temperature, holding or slightly decreasing (more than 5%) the amount of stretch, to allow the film to anneal. The latter step imparts the low TD shrink characteristics of the films described herein. Thus, for example, where the pre-heat temperature is 120 °C, the stretch temperature may be 114 °C, and the cooling step may be 98 °C, or any temperature within the ranges disclosed. The steps are carried out for a sufficient time to affect the desired film properties as those skilled in the art will understand.

[0048] Thus, in certain embodiments the film(s) described herein are biaxially oriented with at least a 5 or 6 or 7 or 8-fold TD orientation and at least a 2 or 3 or 4-fold MD orientation. Being so formed, the at least three-layer (one core, two skin layers, 18-21 μm thickness) possess an ultimate tensile strength within the range of from 100 or 110 to 80 or 90 or 200 MPa in the TD in certain embodiments; and possess an ultimate tensile strength within the range of from 30 or 40 to 150 or 130 MPa in the MD in other embodiments. Further, the SCS films described herein possess an MD Elmendorf tear is greater than 10 or 15 g in certain embodiments, and the 25 TD Elmendorf tear is greater than 15 or 20 g in other embodiments.

INDUSTRIAL APPLICABILITY

[0049] The disclosed multilayered films may be stand-alone films, laminates, or webs. Or, the multilayered films may be sealed, coated, metallized, and/or laminated to other film structures. The laminating substrate, itself, may for instance, be a BOPE or a non-oriented, cast or blown PE film with or without the assistance of adhesive(s), increases in temperature and/or pressure, water or solvents, etc.; furthermore, the laminating substrate may or may not be metallized and/or coated. The disclosed multilayered films may be prepared by any suitable methods comprising the steps of co-extruding a multilayered film according to the description and claims of this specification, orienting and preparing the film for intended use such as by coating, printing, slitting, or other converting methods.

[0050] For some applications, it may be desirable to laminate the multilayered films to other polymeric film or paper products for purposes such as package decor including printing and metallizing. These activities are typically performed by the ultimate end-users or film converters who process films for supply to the ultimate end-users.

[0051] The prepared multilayered film may be used as a flexible packaging film to package an article or good, such as a food item or other product. In some applications, the film may be formed into a pouch type of package, such as may be useful for packaging a beverage, liquid, granular, or dry-powder product.

EXAMPLE EMBODIMENTS

[0052] The following are example, produced films in line with the foregoing disclosure:

EXAMPLE 1

skin	LLDPE (*e.g.*, Prime Polymer SP3022) + antiblock (*e.g.*, silica) and slip (*e.g.*, Erucamide)
core	HDPE (*e.g.*, NOAV 19A or Exxon HTA108)
printable layer	LLDPE (*e.g.*, Prime Polymer SP3022) + antiblock (*e.g.*, silica)

EXAMPLE 2

skin	EP copolymer (*e.g.*, KS407) + antiblock (*e.g.*, silica) and slip (*e.g.*, Erucamide)
core	HDPE (*e.g.*, NOAV 19A or Exxon HTA108) + 20% LLDPE (*e.g.*, Prime Polymer SP3022)
printable layer	EP copolymer (*e.g.*, KS407) + antiblock (*e.g.*, silica)

[0053] In example 1, metallocene LLDPE was used, but other type(s) of LLDPE(s) may be used, whether formed under non-metallocene chemistry, *e.g.*, employing lanthanides or actinides, or metallocene catalysis. Here, the Prime Polymer SP3022 had a density and melt index of 0.927 g/cm^3 and 1.9, respectively. The core of example 1 comprises, consists essentially of, or consists of HDPE(s), wherein NOAV 19A and Exxon HTA108 have densities and melt indices of 0.962 g/cm^3 and 0.72 and 0.961 g/cm^3 and 0.70, respectively. In other example embodiments, the core may comprise, consist essentially of, or consist of PE(s) having a density $\geq$ 0.94 g/cm^3.

[0054] Turning to example 2, an EP copolymer was used in the film's skin and printable layers. The core comprises, consists essentially of, or consists of HDPE(s) in combination with 20% by weight of LLDPE(s). In other example embodiments, the HDPE(s) may

constitute 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 98 percent by weight in combination with 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, or 2 percent by weight of LLDPE(s). In such mixtures, the combinations of percent weights or HDPE(s) and LLDPE(s) may or may not add up to 100 as the core may or may not include other substances.

[0055] Examples 1 and 2 were oriented 4.5 times in the machine direction at 100ºC and 8-10 times in the transverse direction at 115ºC. After stretching, both of these films were 20 μm in thickness. In other embodiments, the films may be thinner or thicker.

[0056] Subsequent to biaxial orientation, mechanical properties of examples 1 and 2 were measured, wherein the results are stated in the following table:

	Modulus (MPa)	**Stress at Break (MPa)**	**Strain at Break (%)**
Example 1 - MD	1427	106	263
Example 1 - TD	1571	117	60
Example 2 - MD	1245	74	196
Example 2 - TD	1436	97	83

Table 1

Comparatively, if the foregoing biaxially oriented examples 1 and 2 contained LLDPE in the skin, core and printable layers instead of the LLDPE/HDPE/LLDPE composition of example 1 and the EP copolymer/(HDPE + 20% LLDPE)/EP copolymer of example 2 (*i.e.*, "LLDPE reference"), then the results would be:

	Modulus (MPa)	Stress at Break (MPa)	Strain at Break (%)
LLDPE reference - MD	299	57	380
LLDPE reference - TD	500	74	186

Table 2

[0057] Subsequent to biaxial orientation of examples 1 and 2 and placing in an over for 7 minutes, dimensional stabilities at the stated temperatures were measured, wherein the results are stated in the following table:

	100°C	110°C	120°C
LLDPE reference - MD	-5.1	-9.0	-19.2
LLDPE reference - TD	-6.5	-13.3	-34.5
Example 1 - MD	-.05	-0.7	-1.7
Example 1 - TD	0.0	0.0	0.4
Example 2 - MD	-0.1	-0.6	-0.6
Example 2 - TD	-0.1	-0.3	-0.5

Table 3

[0058] Dimensional stability tests involve placing a film sample of known original dimensions into a temperature-controlled convection oven for a certain period of time and measuring the length of the sample after such conditioning. Results are reported as % change. Negative numbers indicate shrinkage, while positive numbers indicate expansion.

[0059] Haze of the LLDPE reference and examples 1 and 2 were measured to be 6%, 25%, and 7%, respectively.

[0060] The modulus data shows that films having an HDPE core have mechanical properties that are stiffer and/or more conducive to printing than those with lower moduli. Furthermore, the HDPE film has good dimensional stability, which means that a laminate may seal at a broader temperature range before distorting the seal.

[0061] The LLDPE reference and the example 1 were laminated to a transparent substrate, a sealant BOPE film, and a metallized sealant BOPE film through adhesive lamination. Sealing strengths were measured on the laminated compositions/structures after using an Otto Bruger sealant equipment with a dwell time of 0.75 s and a jaw pressure of 41 N/cm^2. These sealing strengths are reported in g/inch in the following table:

	80°C	**90°C**	**100°C**	**110°C**	**120°C**	**130°C**
LLDPE reference/metallized BOPE film	140	1560	1660	1040	2070	
Example 1/metallized BOPE film	190	1590	1460	1160	1320	2020
LLDPE reference/transparent BOPE film	0	150	2120	2900	3020	
Example 1/transparent BOPE film	0	270	2540	3260	3730	2670

Table 4

The LLDPE reference/metallized BOPE and LLDPE reference/transparent BOPE film exhibited shrinking at 120°C and melting at 130°C. Example 1/metallized BOPE film and example 1/transparent BOPE film exhibited melting at 140°C.

[0062] Bags were produced. Specifically, bags were produced on a vertical-form-fill-seal ("VFFS") machine having transversal and longitudinal jaws at 130°C. All PE laminates used a lap seal, *i.e.*, the outside web is sealed against the inside web to form the longitudinal seal. Hermeticity was excellent, *i.e.*, there were no leaks when the bags were pushed by hand under water.

[0063] The bags were tested for drop resistance. Specifically, ten 450 g bags were dropped from a height of two meters. None of the bags in Table 4 opened, whereas had the bags would have opened if the outside web had been PET or BOPP instead of the LLDPE reference or examples 1 or 2.

[0064] In closing, it is noted that examples 1 or 2 in the laminate are stiffer than bags made with the LLDPE reference as the outside web. And as previously suggested, all-PE laminated bags can be recycled, whereas bags made with BOPP or PET as outside web and PE as sealant web would not be recyclable.

[0065] While the foregoing is directed to example embodiments of the disclosed invention, other and further embodiments may be devised without departing from the basic scope thereof, wherein the scope of the disclosed compositions, systems and methods are determined by one or more claims.

What is claimed is:

1. A transparent film comprising:

a core comprising at least 50 wt.% high-density polyethylene;

a printable skin layer adjacent to a first side of the core;

a skin layer adjacent to a second side of the core,

wherein the transparent film is oriented in at least one direction and has a directional modulus of at least 1200 MPa.

2. The transparent film of claim 1, wherein the printable skin layer consists essentially of linear low-density polyethylene or ethylene-propylene copolymer.
3. The transparent film of claim 1, wherein the skin layer consists essentially of linear low-density polyethylene or ethylene-propylene copolymer.
4. The transparent film of claim 1, further comprising 50 wt.% or less of linear low-density polyethylene.
5. The transparent film of claim 1, further comprising one or more additives.
6. The transparent film of claim 1, further comprising one or more tie layers.
7. The transparent film of claim 1, wherein the transparent film has a thickness of 20 μm or less.
8. The transparent film of claim 1, wherein the transparent film has a haze of 10% or less.
9. The transparent film of claim 1, wherein the transparent film has a dimensional stability of less than 10% after 7 minutes in an oven at 100°C.
10. The transparent film of claim 1, wherein the transparent film withstands directional stress of at least 70 MPa.

11. The transparent film of claim 1, wherein the transparent film withstands directional strain of at least 60 MPa.
12. The transparent film of claim 1, wherein the transparent film is coextruded.
13. The transparent film of claim 1, further comprising a laminating substrate, wherein the transparent film is laminated to the laminating substrate to produce a laminated film.
14. The transparent film of claim 13, wherein the laminating substrate is transparent.
15. The transparent film of claim 13, wherein the laminating substrate is a non-oriented film.
16. The transparent film of claim 13, wherein the laminating substrate is metallized.
17. The transparent film of claim 13, wherein the laminating substrate is coated.
18. The transparent film of claim 13, further comprising an adhesive between the transparent film and the laminating substrate.
19. The transparent film of claim 13, wherein the laminated film has a seal strength of at least 2000 g/inch at 130°C.
20. The transparent film of claim 13, wherein a 450-gram bag of the laminated film dropped from two meters remains intact.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 18/63695

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09D 5/24, G02B 5/22, G06F 1/16 (2019.01)
CPC - C09D 5/24, C09D 7/70, G02B 1/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2016/0031191 A1 (Toray Plastics (America) Inc.) 4 February 2016 (04.02.2016) Abstract, para [0008], [0011], [0013], [0015]-[0016], [0020], [0026], [0028], [0042]-[0045], and Table 1.	1, 3, 5, 7-12 ---------- 2, 4, 6, 13-20
Y	Zhang, et al. "Oriented structure and anisotropy properties of polymer blown films: HDPE, LLDPE and LDPE." Polymer 45.1 (1 January 2004): 217-229. pg 217 col 1 para 1, pg 217 col 2 para 1, and Table 5.	2, 4
Y	US 2015/0183980 A1 (Evergreen Packaging, Inc.) 2 July 2015 (02.07.2015) Abstract, para [0011], [0018], Figure 1A, and Figure 2.	6
Y	Mueller, et al. "Thin laminate films for barrier packaging application-influence of down gauging and substrate surface properties on the permeation properties." Packaging Technology and Science 25.3 (April 2012): 137-148. Abstract; pg 139 para 7; pg 141 para 1, para 4, para 6; pg 146 para 4, and Table 3.	13-20
A	US 2013/0209756 A1 (Squier et al.) 15 August 2013 (15.08.2013) Entire Document.	1-20
A	US 5,885,721 A (Su et al.) 23 March 1999 (23.03.1999) Entire Document.	1-20
A	US 2002/0098334 A1 (Robert V. Poirier) 25 July 2002 (25.07.2002) Entire Document.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search	Date of mailing of the international search report
1 February 2019	08 MAR 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774