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(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, Michigan 48674 (US).

(72) Inventors; and

(71) Applicants *(for BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG only)*: **LIN, Yijian** [CN/US]; Apt. #7104, 3800 Country Road 94, Manvel, Texas 77578 (US). **DEMIRORS, Mehmet** [US/US]; 2319 Bending Spring Dr., Pearland, Texas 77584 (US). **PING, Jian** [CN/CN]; Room 501, No. 3, Lane 418, Mudan Rd., Pudong, Shanghai 200135 (CN). **YUN, Xiaobing** [CN/CN]; Number 8 Nanxiange Street, Xuanwu District, Beijing 100053 (CN).

(74) Agent: **WU, FENG & ZHANG CO.**; Room 305, Tower B, BEIJING AEROSPACE CPMIEC BUILDING, No.30 Haidian South Road, Haidian District, Beijing 100080 (CN).

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(54) Title: ORIENTED POLYETHYLENE FILMS AND A METHOD FOR MAKING THE SAME

(57) Abstract: A first oriented film comprising a first polyethylene composition which comprises: from20 to 50wt% of a first linear low density polyethylene polymer having a density greater than 0.925g/cc and an I_2 lower than 2g/10 min; and from 80 to 50wt% of a second linear low density polyethylene polymer having a density lower than or equal to 0.925g/cc and an I_2 greater than or equal to 2g/10min; wherein the first polyethylene composition has an I_2 from 0.5 to 10g/10min and a density from 0.910 to 0.940g/cc is provided.

ORIENTED POLYETHYLENE FILMS AND A METHOD FOR MAKING THE SAME

Field of Invention

The instant invention relates to oriented polyethylene films and a method for making the same.

Background of the Invention

Tenter frame sequential biaxial orientation process is one of the common fabrication processes in the polymer film industry. In this process, polymers are oriented in the semi-solid state, which is significantly different from the orientation in the molten state, as occurs in traditional blown film or cast film processes. Most physical properties, including clarity, stiffness and toughness, are dramatically improved upon the semi-solid state orientation.Polymers that can be processed by the tenter frame include polypropylene (PP), polyethylene terephthalate (PET), and polyamide (PA). However, currently available polyethylenes cannot be oriented by the tenter frame process, due to their poor stretchability.

Summary of the Invention

The instant invention includes oriented polyethylene films and a method for making the same.

In one embodiment, the instant invention provides a first oriented film comprising a first polyethylene composition which comprises: from 20 to 50 wt% of a first linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 lower than 2 g/10min; and from 80 to 50 wt% of a second linear low density polyethylene polymer having a density lower than 0.925 g/cc and an I_2 greater than 2 g/10min;wherein the first polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

Detailed Description of the Invention

The instant invention includes oriented polyethylene films and a method for making the same.

A first embodiment provides a first oriented film comprising a first polyethylene composition which comprises: from 20 to 50 wt% of a first linear low density polyethylene polymer having a density greater than or equal to 0.925 g/cc and an I_2 lower than or equal to 2 g/10min; and from 80 to 50 wt% of a second linear low density polyethylene polymer having a density lower than or equal to 0.925 g/cc and an I_2 greater than or equal to 2 g/10min;wherein the first polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

The first polyethylene composition comprises from 20 to 50 wt% of a first linear low density polyethylene polymer. All individual values and subranges from 20 to 50 percent by weight (wt%) are included herein and disclosed herein; for example the amount of the first linear low density polyethylene polymer can be from a lower limit of 20, 30, or 40 wt% to an upper limit of 25, 35, 45, or 50 wt%. For example, the amount of the first linear low density polyethylene polymer can be from 20 to 50 wt%, or in the alternative, from 20 to 35 wt%, or in the alternative, from 35 to 50 wt%, or in the alternative from 25 to 45wt%.

The first linear low density polyethylene polymer has a density greater than or equal to0.925 g/cc. All individual values and subranges greater than or equal to 0.925 g/cc are included herein and disclosed herein; for example, the density of the first linear low density polyethylene polymer can be from a lower limit of 0.925, 0.928, 0.931 or 0.34 g/cc. In some aspects of the invention, the first linear low density polyethylene polymer has a density less than or equal to 0.98 g/cc. All individual values and subranges of less than 0.98 are included herein and disclosed herein; for example, the first linear low density polyethylene polymer can have a density from an upper limit of 0.98, 0.97, 0.96 or 0.95 g/cc.

The first linear low density polyethylene polymer has an I_2less than or equal to2 g/10min. All individual values and subranges from 2 g/10min are included herein and disclosed herein. For example, the first linear low density polyethylene polymer can have a density from an upper limit of 2, 1.9, 1.8, 1.7, 1.6 or 1.5 g/10min. In a particular aspect of the invention, the first linear low density polyethylene polymer has an I_2 with a lower limit of 0.01 g/10min. All individual values and subranges from 0.01 g/10min are included herein and disclosed herein. For examples the first linear low density polyethylene polymer can have an I_2 greater than or equal to 0.01, 0.05, 0.1, 0.15 g/10min.

The first polyethylene composition comprises from 80 to 50 wt% of a second linear low density polyethylene polymer. All individual values and subranges from 80 to 50 wt% are included herein and disclosed herein; for example, the amount of the second linear low density polyethylene can be from a lower limit of 50, 60 or 70 wt% to an upper limit of 55, 65, 75 or 80 wt%. For example, the amount of the second linear low density polyethylene polymer can be from 80 to 50 wt%, or in the alternative, from 80 to 60 wt%, or in the alternative, from 70 to 50 wt% , or in the alternative, from 75 to 60 wt%.

The second linear low density polyethylene polymer has a density lower than or equal to 0.925 g/cc. All individual values and subranges lower than or equal to 0.925 g/cc are included herein and disclosed herein; for example, the density of the second linear low density polyethylene polymer can have an upper limit of 0.925, 0.921, 0.918, 0.915, 0.911, or 0.905 g/cc. In a particular aspect, the density of the second linear low density polyethylene polymer can have a lower limit of 0.865 g/cc. All individual values and subranges equal to or greater than 0.865 g/cc are included herein and disclosed herein; for example, the density of the second linear low density polyethylene polymer can have a lower limit of 0.865, 0.868, 0.872, or 0.875 g/cc.

The second linear low density polyethylene polymer has an I_2 greater than or equal to 2 g/10min. All individual values and subranges from 2 g/10min are included herein and disclosed herein; for example, the I_2 of the second linear low density polyethylene polymer can have a lower limit of 2, 2.5, 5, 7.5 or 10 g/10min. In a particular aspect, the second linear low density polyethylene polymer has an I_2 of less than or equal to 1000 g/10 min.

The first polyethylene composition has an I_2 from 0.5 to 10 g/10min. All individual values and subranges from 0.5 to 10 g/10min are included herein and disclosed herein; for example the I_2 of the first polyethylene composition can be from a lower limit of 0.5, 1, 4, 7, or 9 g/10min to an upper limit of 0.8, 1.6, 5, 8 or 10 g/10 min. For example the I_2 of the first polyethylene composition can be from 0.5 to 10 g/10min, or in the alternative, from 0.5 to 5 g/10min, or in the alternative, from 5 to 10 g/10min, or in the alternative, from 2 to 8 g/10min, or in the alternative, from 3 to 7 g/10min.

The first polyethylene composition has a density from 0.910 to 0.940 g/cc. All individual values and subranges from 0.910 to 0.940 g/cc are included herein and disclosed herein; for example, the density of the first polyethylene composition can be from a lower limit of 0.91, 0.92, or 0.93 g/cc to an upper limit of 0.915, 0.925, 0.935 or 0.94 g/cc. For example, the density of the first polyethylene composition can be from 0.910 to 0.940 g/cc, or in the alternative, from 0.91 to 0.925 g/cc, or in the alternative, from 0.925 to 0.94 g/cc, or in the alternative, from 0.92 to 0.935 g/cc.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the first and/or second linear low density polyethylene polymer(s) is produced using a Ziegler-Natta catalyst.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the first linear low density polyethylene polymer has a density greater than or equal to 0.930 g/cc and an I_2 lower than 1 g/10min.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the second linear low density polyethylene polymer has a density less than 0.920 g/cc and an I_2 greater than 4 g/10min.

In another embodiment, the invention provides a second oriented film comprising a second polyethylene composition which comprises: from 50 to 80 wt% of a third linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 less than 2 g/10min; and from 50 to 20 wt% of a fourth linear low density polyethylene polymer having a density lower than 0.920 g/cc and an I_2 greater than 2 g/10min;wherein the second polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

The second polyethylene composition comprises from 50 to 80 wt% of a third linear low density polyethylene polymer. All individual values and subranges from 50 to 80 wt% are included herein and disclosed herein; for example, the amount of third linear low density polyethylene polymer can be from a lower limit of 50, 60, or 70 wt% to an upper limit of 55, 65, 75 or 80 wt%. For example, the amount of the third linear low density polyethylene polymer can be from 50 to 80 wt%, or in the alternative, from 60 to 80 wt%, or in the alternative, from 55 to 80 wt%, or in the alternative, from 60 to 70 wt%.

The third linear low density polyethylene polymer has a density greater than or equal to0.925 g/cc. All individual values and subranges greater than 0.925 g/cc are included herein and disclosed herein; for example, the density of the third linear low density polyethylene polymer can have a lower limit of 0.925, 0.928, 0.931, 0.934, 0.939 or 0.943 g/cc. In a particular embodiment, the third linear low density polyethylene polymer has a density less than or equal to 0.98 g/cc. All individual values and subranges less than or equal to 0.98 g/cc are included herein and disclosed herein; for example the upper limit of the density of the third linear low density polyethylene polymer can be 0.98, 0.97, 0.965, 0.962, 0.955, or 0.951 g/cc.

The third linear low density polyethylene polymer has an I_2 less than or equal to 2 g/10min. All individual values and subranges less than 2 g/10min are included herein and disclosed herein; for example, the upper limit of the $I_2$of the third linear low density polyethylene polymer can be from an upper limit of 2, 1.7, 1.4, 1.1 or 0.9 g/10min. In a particular embodiment, the $I_2$of the third linear low density polyethylene polymer is greater than or equal to 0.01 g/10min. All individual values and subranges greater than 0.01 g/10min are included herein and disclosed herein; for example the lower

limit of the $I_2$of the third linear low density polyethylene polymer can be 0.01, 0.05, 0.1, 0.15 g/10min.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the third linear low density polyethylene polymer is produced using a Ziegler-Natta catalyst.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the fourth linear low density polyethylene polymer is produced using a molecular catalyst. Molecular catalyst are homogeneous polymerization catalysts which comprise (a) a transition metal, (b) one or more non-substituted or substituted cyclopentadienyl ligands, and/or (c) one or more ligands containing at least one heteroatom, such as, oxygen, nitrogen, phosphorus, and/or sulfur. Molecular catalyst may be immobilized on an inorganic support, such as silica, alumina, or $MgCl_2$.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the third linear low density polyethylene polymer has a density greater than 0.930 g/cc and an I_2 lower than 1 g/10min.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the fourth linear low density polyethylene polymer has a density less than 0.915 g/cc and an I_2 greater than 4 g/10min.

In another embodiment, the invention provides a third oriented film comprising a third polyethylene composition which comprises from 75 to less than 100 wt% of the first polyethylene composition according to any embodiment disclosed herein and/or the second polyethylene composition according to any embodiment disclosed herein; and greater than 0 to 25 wt% of at least one ethylene-based or propylene-based polymer. The third oriented film comprises a third polyethylene composition which comprises from 75 to less than 100 wt% of the first polyethylene composition according to any embodiment disclosed herein. All individual values and subranges from 75 to less than 100 wt% are included herein and disclosed herein. For example, the amount of the first polyethylene composition in the third polyethylene composition can be from a lower limit of 75, 80, 85, 90, or 95 wt% to an upper limit of 99.99, 99, 98, 93, 89, 84 or 80 wt%. For example, the amount of the first polyethylene composition in the third polyethylene composition can be from 75 to less than 100 wt%, or in the alternative, from 80 to 99 wt%, or in the alternative, from 84 to 99.99 wt%, or in the alternative, from 80 to 90 wt%.

The third polyethylene composition comprises greater than 0 to 25 wt% of at least one ethylene-based or propylene-based polymer. All individual values and subranges from greater than 0 to 25 wt% are included herein and disclosed herein; for example, the amount of the at least one ethylene-based or propylene-based polymer can be from a lower limit of 0.01, 0.5, 1, 8, 14, 19 or 24 wt% to an upper limit of 0.8, 3, 10, 15, 20 or 25 wt%. For example, the amount of the at least one ethylene-based or propylene-based polymer can be from greater than 0 to 25 wt%, or in the alternative, from 1 to 15 wt%, or in the alternative, from 16 to 25 wt%, or in the alternative, from 5 to 20 wt%.

The term "ethylene-based polymer," as used herein,refers to a polymer that comprises, in polymerized form, a majority amount of ethylene monomer (based on the weight of the polymer), and optionally may comprise one or more comonomers. Exemplary ethylene-based polymers include low density polyethylene (LDPE, e.g., LDPE having a density from 0.917 to 0.924 g/ccand an I_2 of from 0.2 to 75 g/10 min),linear low density polyethylene (LLDPE, e.g., DOWLEX which is an ethylene/1-octene polyethylene made by The Dow Chemical Company with a typical density between about 0.915 and 0.940 g/cc and a typical I_2 between about 0.5 and 30 g/10 min), homogeneously branched, linear ethylene/alpha-olefin copolymers (e.g., TAFMER polymers by Mitsui Chemicals America, Inc. and EXACT polymers by ExxonMobil Chemical (ExxonMobil)), homogeneously branched, substantially linear ethylene/alpha-olefin polymers (e.g., AFFINITY and ENGAGE polymers made by The Dow Chemical Company and described in U.S. Pat. No. 5,272,236, U.S. Pat.No. 5,278,272 and U.S. Pat. No. 5,380,810, the disclosures of which are incorporated herein by reference), catalytic linear statistical olefin copolymers (e.g., INFUSE which are polyethylene/olefin block polymers, particularly polyethylene/alpha-olefin block polymers and especially polyethylene/1-octene block polymers, made by The Dow Chemical Company and described in WO 2005/090425, 2005/090426 and 2005/090427, the disclosures of which are incorporated herein by reference), and high pressure, free radical polymerized ethylene copolymers such as ethylene/vinyl acetate (EVA) and ethylene/acrylate and ethylene/methacrylate polymers (e.g., ELVAX. and ELVALOY polymers, respectively, commercially available from E. I. Du Pont du Nemours & Co. (Du Pont)) and ethylene/acrylic (EAA) and ethylene/methacrylic acid (EMAA)polymers (e.g., PRIMACOR EAA polymers commercially available from The Dow Chemical Company and NUCREL EMAA polymers commercially available from Du Pont).

The term "propylene-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, a majority amount of units derived from propylene monomer (based on the weight of the polymer), and optionally may comprise one or more comonomers. Exemplary propylene-based polymers include those available under the tradename VERSIFY, commercially available from The Dow Chemical Company.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the first oriented film according to claim 1, wherein the first polyethylene composition has $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the second oriented film according to claim 6, wherein the first polyethylene composition has $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

The invention further provides the third oriented film according to any embodiment disclosed herein except that the first polyethylene composition has $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the first oriented film according to any embodiment disclosed herein, wherein the first oriented film is oriented below the melting point of the first polyethylene composition.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the second oriented film according to any embodiment disclosed herein, wherein the second oriented film is oriented below the melting point of the second polyethylene composition,

The invention further provides the third oriented film according to any embodiment disclosed herein except that the third oriented film according to any embodiment disclosed herein, wherein the third oriented film is oriented below the melting point of the third polyethylene composition.

The invention further provides the first oriented film according to any embodiment disclosed herein except that the first oriented film is a biaxially oriented film.

The invention further provides the second oriented film according to any embodiment disclosed herein except that the second oriented film is a biaxially oriented film.

The invention further provides the third oriented film according to any embodiment disclosed herein except that the third oriented film is a biaxially oriented film.

The invention further provides the first biaxially oriented film according to any embodiment disclosed herein except that the first biaxially oriented film has been oriented via a sequential orientation process with a machine direction (MD) draw ratio greater than 3 and a transverse direction (TD) draw ratio greater than 5.

The invention further provides the second biaxially oriented film according to any embodiment disclosed herein except that the second biaxially oriented film has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

The invention further provides the third biaxially oriented film according to any embodiment disclosed herein except that the third biaxially oriented film has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

With respect to each of the first, second and third biaxially oriented films, all individual values and subranges of an MD draw ratio equal to or greater than 3 are included herein and disclosed herein. For example, the MD draw ratio can be equal to or greater than 3, 3.5, 4, 4.5 or 5. In a particular embodiment, the MD draw ratio is equal to or less than 8. All individual values and subranges of equal to or less than 8 are included herein and disclosed herein; for example, the MD draw ratio can be from an upper limit of 8, 7, or 6.

With respect to each of the first, second and third biaxially oriented films, all individual values and subranges of a TD draw ratio greater than 5 are included herein and disclosed herein. For example, the TD draw ratio can be greater than 5, 5.5, 6, 6.5 or 7. In a particular embodiment, the TD draw ratio is equal to or less than 13. All individual values and subranges of equal to or less than 13 are included herein and disclosed herein; for example, the TD draw ratio can be from an upper limit of 13, 12, 11, 10, 9 or 8.

The invention further provides the first biaxially oriented film according to any embodiment disclosed herein except that the first biaxially oriented film has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.In a particular embodiment, the MD draw ratio has an upper limit of 8 and a TD draw ratio upper limit of 8.

The invention further provides the second biaxially oriented film according to any embodiment disclosed herein except that the second biaxially oriented film has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater

than 4. In a particular embodiment, the MD draw ratio has an upper limit of 8 and a TD draw ratio upper limit of 8.

The invention further provides the third biaxially oriented film according to any embodiment disclosed herein except that the third biaxially oriented film has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4. In a particular embodiment, the MD draw ratio has an upper limit of 8 and a TD draw ratio upper limit of 8.

In yet another aspect the invention provides a first co-extruded film comprising at least one film layer comprising the first oriented film according to any embodiment disclosed herein.

In yet another aspect the invention provides a first laminated film comprising at least one film layer comprising the first oriented film according to any embodiment disclosed herein.

In yet another aspect the invention provides a second co-extruded film comprising at least one film layer comprising the second oriented film according to any embodiment disclosed herein.

In yet another aspect the invention provides a second laminated film comprising at least one film layer comprising the second oriented film according to any embodiment disclosed herein.

In yet another aspect the invention provides a third co-extruded film comprising at least one film layer comprising the third oriented film according to any embodiment disclosed herein.

In yet another aspect the invention provides a third laminated film comprising at least one film layer comprising the third oriented film according to any embodiment disclosed herein.

In yet another embodiment, the present disclosure provides a first oriented film in accordance with any of the embodiments disclosed herein except that the first oriented film exhibits one or more of the following properties: (a) ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and (b) 2% secant modulus averaged in MD and TD, measured according to ASTM D882, is greater than or equal to 350MPa. All individual values and subranges of an averaged ultimate tensile strength greater than or equal to 40MPa are included herein and disclosed herein; for example, the averaged ultimate tensile strength of the first oriented film can be greater than or equal to 40MPa, or in the alternative, from greater than or equal to 75Mpa, or in the alternative, from greater than or equal to 100 MPa. All individual values and subranges of an averaged 2% secant modulus greater than or equal to 350MPa are included herein and disclosed herein; for example, the averaged 2% secant modulus of the first

oriented film can be greater than or equal to 350MPa, or in the alternative, from greater than or equal to 750 MPa, or in the alternative, from greater than or equal to 1000 MPa.

In yet another embodiment, the present disclosure provides a second oriented film in accordance with any of the embodiments disclosed herein except that the second oriented film exhibits one or more of the following properties: (a) ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and (b) 2% secant modulus averaged in MD and TD, measured according to ASTM D882, is greater than or equal to 350MPa. All individual values and subranges of an averaged ultimate tensile strength greater than or equal to 40MPa are included herein and disclosed herein; for example, the averaged ultimate tensile strength of the second oriented film can be greater than or equal to 40MPa, or in the alternative, from greater than or equal to 75MPa, or in the alternafirtive, from greater than or equal to 100 MPa. All individual values and subranges of an averaged 2% secant modulus greater than or equal to 350MPa are included herein and disclosed herein; for example, the averaged 2% secant modulus of the second oriented film can be greater than or equal to 350MPa, or in the alternative, from greater than or equal to 750 Mpa, or in the alternative, from greater than or equal to 1000 MPa.

In yet another embodiment, the present disclosure provides a third oriented film in accordance with any of the embodiments disclosed herein except that the third oriented film exhibits one or more of the following properties: (a) ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and (b) 2% secant modulus averaged in MD and TD, measured according to ASTM D882, is greater than or equal to 350MPa. All individual values and subranges of an averaged ultimate tensile strength greater than or equal to 40MPa are included herein and disclosed herein; for example, the averaged ultimate tensile strength of the third oriented film can be greater than or equal to 40MPa, or in the alternative, from greater than or equal to 75MPa, or in the alternafirtive, from greater than or equal to 100 MPa. All individual values and subranges of an averaged 2% secant modulus greater than or equal to 350MPa are included herein and disclosed herein; for example, the averaged 2% secant modulus of the third oriented film can be greater than or equal to 350MPa, or in the alternative, from greater than or equal to 750 MPa, or in the alternative, from greater than or equal to 1000 MPa.

In yet another aspect the invention provides a process for forming an oriented polyethylene film comprising (a) selecting the first polyethylene composition according to any embodiment disclosed herein, the second polyethylene composition according to any embodiment disclosed

herein, the third polyethylene composition according to any embodiment disclosed herein or any combination thereof; (b) forming a film from the polyethylene composition selected in step (a), (c) orienting the film formed in step (b) via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5. All individual values and subranges of an MD draw ratio greater than 3 are included herein and disclosed herein; for example, the MD draw ration can from a lower limit of 3, 3.5, 4, 4.5 or 5. All individual values and subranges of a TD draw ratio greater than 5 are included herein and disclosed herein; for example, the MD draw ration can from a lower limit of 5, 5.5, 6, 6.5 or 7.

Examples

The following examples illustrate the present invention but are not intended to limit the scope of the invention.

Polyethylene Examples 1-3

Table 1 summarizes the composition of three polyethylenes compositions (PE Comp.) made using a 30 mm co-rotating, intermeshing Coperion Werner-Pfleiderer ZSK-30 twin screw extruder at 250 °C. The ZSK-30 has ten barrel sections with an overall length of 960 mm and an L/D ratio of 32.

PE Polymer 1 is anLLDPE madeusinga Ziegler-Natta(ZN) catalyst and having a density of 0.935 g/cc and an I_2 of 1.0 g/10min;

PE Polymer 2 is anLLDPEmade usinga Ziegler-Natta catalyst and having adensity of 0.935 g/cc and an $I_2$of 2.5 g/10min;

PE Polymer 3 isan LLDPE made using molecular catalyst having a density of 0.905 g/cc and an $I_2$of 15 g/10min;

LDPE 621I is a low density polyethylene having a density of 0.918 g/cc and an I_2 of 2.3 g/10minand is commercially available from The Dow Chemical Company;

LDPE-1is a low density polyethylene having a density of 0.919 g/cc and an I_2 of 0.47 g/10min;and

Affinity PL1880 is a polyolefin plastomer having a density of 0.902 g/cc and an I_2 of 1 g/10min and is commercially available from The Dow Chemical Company.

33-mil cast sheets were made with a Dr. Collin cast film line (L/D = 25 and D = 30mm) equipped with a 12 inch wide flat die. The die gap was 45 mil and output rate was about8 kg/h. Melt temperature was 244 °C and die temperature was set at 260 °C.

Square specimens were cut from the extruded sheet, and biaxially stretched with a Bruckner Karo IV biaxial stretcher at an engineering strain rate of 200%/s based on the original specimen dimensions. The preheat time before stretching was fixed to be 60 s. Stretching was performed either simultaneously in the two directions or sequentially. In simultaneous stretching, the sheet was stretched in both directions to a 6.5x6.5 stretch ratio. In sequential stretching, the specimen was constrained in cross direction and stretched in machine direction to 4x; after that, it was constrained in machine direction at 4x and stretched in transverse direction to 8x.

The cast sheets were also stretched into films with an Accupull stretcher. Only simultaneously biaxial orientation was conducted at 119.4°C and an engineering strain rate of 100%/s. The stretch ratio was 4x8 in MD and TD, respectively. Preheat time was set at 100 s.

In the blown film process,1 mil monolayer blown film was made using the 3-layer Dr. Collin blown film line. The line was comprised of three 25:1 L/D single screw extruders, equipped with grooved feed zones. The screw diameters were 25 mm for the inner layer, 30 mm for the core and 25 mm for the outer layer. The annular die was 60 mm in diameter and used a dual lip air ring cooling system. Die lip gap was set at 2 mm. Blow up ratio (BUR) was 2.5 and draw down ratio (DDR) was 31.5. Frost line height was 6 inch. Total output rate was around 10.7 kg/hour. Melt temperature and die temperature were set at 215 °C.

Table 1

PE Comp. Ex.	Component 1	Component 2	Component 3	Density (g/cc)	I_2 (g/10 min)	$MW_{HDF>95}$ (kg/mol)	$I_{HDF>95}$ (kg/mol)
1	70 wt% PE Polymer 1	30 wt% PE Polymer 3	None	0.927	1.6	145	65.8
2	55 wt% PE Polymer 1	30 wt% PE Polymer 3	7.5 wt% LDPE 621I; and 7.5 wt% LDPE-1	0.926	1.5	152	54.9
3	55 wt% PE Polymer 2	30 wt% Affinity PL1880	15 wt% LDPE 621I	0.925	1.6	127	37.9

PE Composition Examples 1 and 2 were used to produce BOPE films. BOPE films could not be made from PE Composition Example 3. Biaxial stretchability of the samples was evaluated on a lab-scale tenter frame stretcher (Bruckner Karo IV). Results of simultaneous stretching and

sequential stretching are summarized in Tables 2 and 3 where S means Succeed, F means Fail, and N means Not Tested. The success criterion for the simultaneous stretching is to achieve 6.5x stretch ratio in both MD and TD. The success criterion for the sequential stretching is to achieve 4x stretch ratio in MD and 8 x in TD. Inventive Films 1 and 2 clearly show a good stretchability and a broad stretching temperature window.

Table 2

Oven temperature (°C)	**105**	**108**	**110**	**113**	**115**	**117**	**118**	**120**	**123**	**125**	**127**	**130**
PE Comp. Ex. 1	N	N	N	N	N	N	F	S	S	S	F	N
PE Comp. Ex. 2	N	N	N	N	F	S	S	S	S	F	N	N
PE Comp. Ex. 3	F	F	F	F	F	F	F	F	F	F	F	F

Table 3

Oven temperature (°C)	**105**	**108**	**110**	**113**	**115**	**117**	**118**	**120**	**123**	**125**	**127**	**130**
PE Comp. Ex.1	N	N	N	N	N	N	N	S	F	N	N	N
PE Comp. Ex.2	N	N	N	N	S	S	S	S	F	N	N	N
PE Comp. Ex.3	F	F	F	F	F	F	F	F	F	F	F	F

Table 4

	Raw material	Fabrication process	Process conditions
Inventive Film 1	**PE Comp. Ex. 2**	Tenter frame biaxial orientation on a Bruckner Karo IV stretcher.	Sequentially biaxial orientation. Draw ratio: 4x8 Orientation temperature: 115 °C
Comparative Film 1	**PE Comp. Ex. 2**	Blown film on a Dr. Collin blown film line.	BUR: 2.5 DDR: 31.5
Inventive Film 2	**PE Comp. Ex. 2**	Tenter frame biaxial orientation on aAccupull stretcher.	Simultaneously biaxial orientation. Draw ratio 4x8 Orientation temperature 120 °C

A polyethylene blown film (Comparative film 1), a biaxially oriented polyethylene film sequentially stretched to a draw ratio of 4x8 on the Bruckner stretcher at 115 °C(Inventive Film1), and a biaxially oriented polyethylene film simultaneously stretched to a draw ratio of 4x8 on the Accupull stretcher(Inventive Film 2) and various film properties were tested and reported in Table 5.

Table 5

	Comparative Film 1	Inv. Film 1	Inv. Film 2
Thickness, mil	1	0.9	0.9
Clarity, %	95	99	99
Haze, %	10.6	2.4	2.4
2% secant modulus inTD, MPa	322	1117	569
2% secant modulus in MD, MPa	261	1010	468
2% secant modulus averaged in MD and TD, MPa	292	1064	519
Ultimate tensile strength in TD, MPa	30	153	64
Ultimate tensile strength in MD, MPa	36	135	31
Ultimate tensile strength averaged in MD and TD, MPa	33	144	48
Puncture peak load (N)	26	Not tested	51

Additional PE Compositions were prepared in a dual polymerization reactor system. Table 6 provides the reactor conditions for each of these dual reactor PE Compositions, PE Compositions 4, 5, 6, and 7.The properties of Reactor 2 products were calculated based on the measured properties of the Reactor 1 Products and the Final products according to

$$1/\rho_f = w_1/\rho_1 + w_2/\rho_2$$

$$MI_f^{-0.277} = w_1 MI_1^{-0.277} + w_2 MI_2^{-0.277}$$

where ρ is density, w is weight fraction, MI is melt index (I_2), subscript 1 denotes the reactor 1, subscript 2 denotes the reactor 2 and subscript f denotes the final product.

Tables 6-7 provide certain properties of these PE Compositions. Blends of these PE Compositions 5-7 with a low density polyethylene were also produced, as described in Table 8.

Table 6

	Reactor 1 catalyst	Reactor 1 Product density (g/cc)	Reactor 1 Product I_2 (g/10min)	Reactor 2 catalyst	Reactor 2 Product density (g/cc)*	Reactor 2 Product I_2 (g/10min)	Reactor 1/Reactor 2 split, %	Final product density (g/cc)	Final Product I_2 (g/10 min)
PE Comp. 4	ZN	0.956	0.6	ZN	0.914	3.2	30/70	0.926	1.8
PE Comp. 5	ZN	0.935	0.6	ZN	0.925	3.5	30/70	0.928	1.9
PE Comp. 6	ZN	0.934	0.6	ZN	0.924	5.5	40/60	0.928	1.9
PE Comp. 7	Molecular	0.905	15	ZN	0.939	0.65	35/65	0.927	1.5

* calculated as described below

Table 7

	$MW_{HDF>95}$(kg/mol)	$I_{HDF>95}$(kg/mol)
PE Comp. 4	151	63.4
PE Comp. 5	152	59.3
PE Comp. 6	154	65.8
PE Comp. 7	149	68.1

Table 8

	Composition (in weight %)	**$MW_{HDF>95}$(kg/mol)**	**$I_{HDF>95}$(kg/mol)**
PE Comp. 4-a	85% PE Comp. 4 + 15% LDPE 621I	148	51.3
PE Comp. 5-a	90% PE Comp. 5 + 10% LDPE 621I	158	56.4
PE Comp. 5-b	85% PE Comp. 5 + 15% LDPE 621I	158	53.3
PE Comp. 6-a	90% PE Comp. 6 + 10% LDPE 621I	156	59.0
PE Comp. 6-b	85% PE Comp. 6 + 15% LDPE 621I	158	59.7
PE Comp. 7-a	90% PE Comp. 7 + 10% LDPE 621I	150	61.9
PE Comp. 7-b	85% PE Comp. 7 + 15% LDPE 621I	153	60.9

Table 9 provides the simultaneously biaxial orientation results (tested by the Bruckner biaxial stretcher) for films using a MD draw ratio of 6.5x and a TD draw ratio of 6.5xproduced using several of the PE Compositions shown in Tables 6 and 8.

Table 9

Oven temperature (°C)	**110**	**113**	**115**	**117**	**120**	**122**	**125**	**127**
Inventive Film 4-a	N	F	S	S	S	S	S	F
Inventive Film 5	N	F	F	F	S	S	F	N
Inventive Film 5-a	N	F	F	S	S	S	F	N
Inventive Film 5-b	F	F	F	S	S	S	F	N
Inventive Film 6	N	F	F	F	F	S	F	N
Inventive Film 6-a	N	F	F	F	S	S	F	N
Inventive Film 6-b	F	F	S	S	S	S	F	N
Inventive Film 7	N	F	F	F	F	F	S	F
Inventive Film 7-a	N	F	F	F	F	S	F	N
Inventive Film 7-b	F	F	F	F	S	S	F	N

Table 10 provides the sequentially biaxial orientation results (tested by the Bruckner biaxial stretcher) for films using a MD draw ratio of 4x and a TD draw ratio of 8x,produced using several of the PE Compositions shown in Tables 6 and 8.

Table 10

Oven temperature (°C)	110	113	115	117	120	122	125	127
Inventive Film 4-a	N	N	S	S	S	S	S	F
Inventive Film 5-a	N	F	S	S	S	S	F	N
Inventive Film 5-b	N	F	S	S	S	S	F	N
Inventive Film 6-a	N	F	S	S	S	S	S	F
Inventive Film 6-b	N	F	S	S	S	S	S	F
Inventive Film 7-a	N	F	S	S	S	S	S	F
Inventive Film 7-b	N	F	S	S	S	S	S	F

Test Methods

Melt index, or I_2, was measured in accordance with ASTM D 1238, condition 190 °C/2.16 kg. Density was first measured according to ASTM D 1928. Density measurements were made using ASTM D792, Method B.

Tensile properties in both directions were determined using ASTM D882 as was the 2% secant modulus. 2% secant modulus averaged in MD and TD= (2% secant modulus in MD+ 2% secant modulus in TD)/2. Ultimate tensile strength averaged in MD and TD= (Ultimate tensile strength in MD + Ultimate tensile strength in TD)/2. Puncture test was performed using a modified ASTM D 5748 with a 0.5" diameter stainless steel probe.

Film gloss at 20° was determined using ASTM D2457 while haze was done via ASTM D1003 and clarity by ASTM D1746.

Crystallization Elution Fractionation (CEF) is described by Monrabal et al, Macromol. Symp.257, 71-79 (2007). The instrument is equipped with an IR-4 detector (such as that sold commercially from PolymerChar, Spain) and a two angle light scattering detector Model 2040 (such as those sold commercially from Precision Detectors). The IR-4 detector operates in the compositional mode with two filters: C006 and B057. A 10 micron guard column of 50X4.6 mm (such as that sold commercially from PolymerLabs) is installed before the IR-4 detector in the detector oven. Ortho-dichlorobenzene (ODCB, 99% anhydrous grade) and 2,5-di-tert-butyl-4-methylphenol (BHT) (such as commercially available from Sigma-Aldrich) are obtained. Silica gel 40 (particle size 0.2~0.5 mm) (such as commercially available from EMD Chemicals) is also obtained. The silica gel is dried in a vacuum oven at 160°C for about two hours before use. Eight hundred milligrams of BHT and five grams of silica gel are added to two liters of ODCB. ODCB containing BHT and silica gel is now referred to as "ODCB." ODBC is sparged with dried nitrogen

(N_2) for one hour before use. Dried nitrogen is obtained by passing nitrogen at <90 psig over $CaCO_3$ and 5Å molecular sieves. Sample preparation is done with an autosampler at 4 mg/ml under shaking at 160°C for 2 hours. The injection volume is 300 μl. The temperature profile of CEF is: crystallization at 3°C/min from 110°C to 30°C, thermal equilibrium at 30°C for 5 minutes (including Soluble Fraction Elution Time being set as 2 minutes), and elution at 3°C/min from 30°C to 140°C. The flow rate during crystallization is 0.052 ml/min. The flow rate during elution is 0.50 ml/min. The data are collected at one data point/second.

The CEF column is packed with glass beads at 125 μm± 6% (such as those commercially available from MO-SCI Specialty Products) with 1/8 inch stainless tubing according to US 2011/0015346 A1. The internal liquid volume of the CEF column is between 2.1 and 2.3 mL. Temperature calibration is performed by using a mixture of NIST Standard Reference Material Linear polyethylene 1475a (1.0 mg/ml) and Eicosane (2 mg/ml) in ODCB. The calibration consists of four steps: (1) Calculating the delay volume defined as the temperature offset between the measured peak elution temperature of Eicosane minus 30.00°C; (2) Subtracting the temperature offset of the elution temperature from the CEF raw temperature data. It is noted that this temperature offset is a function of experimental conditions, such as elution temperature, elution flow rate, etc.; (3)Creating a linear calibration line transforming the elution temperature across a range of 30.00°C and 140.00°C such that NIST linear polyethylene 1475a has a peak temperature at 101.00°C, and Eicosane has a peak temperature of 30.00°C, (4) For the soluble fraction measured isothermally at 30°C, the elution temperature is extrapolated linearly by using the elution heating rate of 3°C/min. The reported elution peak temperatures are obtained such that the observed comonomer content calibration curve agrees with those previously reported in US 8,372,931.

A linear baseline is calculated by selecting two data points: one before the polymer elutes, usually at temperature of 26°C, and another one after the polymer elutes, usually at 118°C. For each data point, the detector signal is subtracted from the baseline before integration.

Molecular weight of high density fraction ($MW_{HDF>95}$) and high density fraction index ($I_{HDF>95}$)

The polymer molecular weight can be determined directly from LS (light scattering at 90 degree angle, Precision Detectors) and the concentration detector (IR-4, Polymer Char) according to the Rayleigh-Gans-Debys approximation (A. M. Striegel and W. W. Yau, Modern Size-Exclusion Liquid Chromatography, 2nd Edition, Page 242 and Page 263, 2009) by assuming a form factor of 1

and all the virial coefficients equal to zero. Baselines are subtracted from the LS (90 degree) and IR-4 (measurement channel) chromatograms. For the whole resin, integration windows are set to integrate all the chromatograms in the elution temperature (temperature calibration is specified above) ranging from 25.5 to 118 °C. The high density fraction is defined as the fraction that has an elution temperature higher than 95.0°C in CEF. Measuring the $MW_{HDF>95}$ and $I_{HDF>95}$includes the following steps:

(1) Measuring the interdetector offset. The offset is defined as the geometric volume offset between LS detector with respect to the IR-4 detector. It is calculated as the difference in elution volume (mL) of the polymer peak between the IR-4 and LS chromatograms. It is converted to the temperature offset by using the elution thermal rate and elution flow rate. A high density polyethylene (with no comonomer, melting index I_2 of 1.0, polydispersity or molecular weight distribution M_w/M_n approximately 2.6 by conventional gel permeation chromatography) is used. The same experimental conditions as the CEF method above are used except for the following parameters: crystallization at 10°C/min from 140°C to 137°C, thermal equilibrium at 137°C for 1 minute as the Soluble Fraction Elution Time, and elution at 1°C/min from 137°C to 142°C. The flow rate during crystallization is 0.10 ml/min. The flow rate during elution is 0.80 ml/min. The sample concentration is 1.0 mg/ml.

(2) Each data point in the LS chromatogram is shifted to correct for the interdetector offset before integration.

(3) Molecular weight at each retention temperature is calculated as the baseline subtracted LS signal/the baseline subtracted IR4 signal/MW constant (K)

(4) The baseline subtracted LS and IR-4 chromatograms are integrated in the elution temperature range of 95.0 to 118.0°C.

(5) The Molecular weight of the high density fraction ($MW_{HDF>95}$) is calculated according to

$$MW_{HDF>95} = \int_{95}^{118} Mw \cdot C \cdot dT \Big/ \int_{95}^{118} C \cdot dT$$

where Mw is the molecular weight of the polymer fraction at the elution temperature T and C is the weight fraction of the polymer fraction at the elution temperature T in the CEF, and

$$\int_{25}^{118} C \cdot dT = 100\%$$

(6) High density fraction index ($I_{HDF>95}$) is calculated as

$$I_{HDF>95} = \int_{95}^{118} Mw \cdot C \cdot dT$$

Where *Mw* in is the molecular weight of the polymer fraction at the elution temperature *T* in the CEF.

The MW constant (K) of CEF is calculated by using NIST polyethylene 1484a analyzed with the same conditions as for measuring interdetector offset. The MW constant (K) is calculated as "(the total integrated area of LS) of NIST PE1484a /(the total integrated area) of IR-4 measurement channel of NIST PE 1484a /122,000".

The white noise level of the LS detector (90 degree) is calculated from the LS chromatogram prior to the polymer eluting. The LS chromatogram is first corrected for the baseline correction to obtain the baseline subtracted signal. The white noise of the LS is calculated as the standard deviation of the baseline subtracted LS signal by using at least 100 data points prior to the polymer eluting. Typical white noise for LS is 0.20 to 0.35 mV while the whole polymer has a baseline subtracted peak height typically around 170 mV for the high density polyethylene with no comonomer, I_2 of 1.0, polydispersity M_w/M_n approximately 2.6 used in the interdetector offset measurements. Care should be maintained to provide a signal to noise ratio (the peak height of the whole polymer to the white noise) of at least 500 for the high density polyethylene.

CLAIMS

We Claim:

1. A first oriented film comprising a first polyethylene composition which comprises:

from 20 to 50 wt% of a first linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 lower than 2 g/10min; and

from 80 to 50 wt% of a second linear low density polyethylene polymer having a density lower than 0.925 g/cc and an I_2 greater than 2 g/10min;

wherein the first polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

2. The first oriented film according to claim 1, wherein the first and/or second linear low density polyethylene polymer is produced using a Ziegler-Natta catalyst.

4. The first oriented film according to claim 1, wherein the first linear low density polyethylene polymer has a density greater than 0.930 g/cc and an I_2 lower than 1 g/10min.

5. The first oriented film according to claim 1, wherein the second linear low density polyethylene polymer has a density lower than 0.920 g/cc and an I_2 greater than 4 g/10min.

6. A second oriented film comprising a second polyethylene composition which comprises:

from 50 to 80 wt% of a third linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 less than 2 g/10min; and

from 50 to 20 wt% of a fourth linear low density polyethylene polymer having a density lower than 0.920 g/cc and an I_2 greater than 2 g/10min;

wherein the second polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

7. The second oriented film according to claim 6, wherein the third linear low density polyethylene polymer is produced using a Ziegler-Natta catalyst.

8. The second oriented film according to claim 6, wherein the fourth linear low density polyethylene polymer is produced using a molecular catalyst.

10. The second oriented film according to claim 6, wherein the third linear low density polyethylene polymer has a density greater than 0.930 g/cc and an I_2 lower than 1 g/10min.

11. The second oriented film according to claim 6, wherein the fourth linear low density polyethylene polymer has a density less than 0.915 g/cc an I_2 greater than 4 g/10min.

12. A third oriented film comprising a third polyethylene composition comprising:

75 to less than 100 wt% of the first polyethylene composition according to claim 1 and/or the second polyethylene composition according to claim 6; and

greater than 0 to 25 wt% of at least one resin selected from the group consisting of linear low density polyethylene, low density polyethylene, ethylene copolymers, propylene copolymers and high density polyethylene.

13. The first oriented film according to claim 1, wherein the first polyethylene composition has an $MW_{HDF>95}$greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

14. The second oriented film according to claim 6, wherein the first polyethylene composition has an $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

15. The third oriented film according to claim 12, wherein the first polyethylene composition has an $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

16. The first oriented film according to any one of claims 1-5, wherein the first oriented film is oriented below the melting point of the first polyethylene composition.

17. The second oriented film according to any one of claims 6-9, wherein the second oriented film is oriented below the melting point of the second polyethylene composition.

18. The third oriented film according to claim 12, wherein the third oriented film is oriented below the melting point of the third polyethylene composition.

19. The first oriented film according to any one of claims 1-5, wherein the first oriented film is a biaxially oriented film.

20. The second oriented film according to any one of claims 6-9, wherein the second oriented film is a biaxially oriented film.

21. The third oriented film according to claim 12, wherein the third oriented film is a biaxially oriented film.

22. The first biaxially oriented film according to claim 19 which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

23. The second biaxially oriented film according to claim 20 which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

24. The third biaxially oriented film according to claim 21 which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

25. The first biaxially oriented film according to claim 19 which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

26. The second biaxially oriented film according to claim 20 which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

27. The third biaxially oriented film according to claim 21 which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

28. A first co-extruded film comprising at least one film layer comprising the first oriented film according to any one of claims 1-5, 13, 16, 19, 22 and 25.

29. A first laminated film comprising at least one film layer comprising the first oriented film according to any one of claims 1-5, 13, 16, 19, 22 and 25.

30. A second co-extruded film comprising at least one film layer comprising the second oriented film according to any one of claims 6, 14, 20,23 and 26.

31. A second laminated film comprising at least one film layer comprising the second oriented film according to any one of claims 6, 14, 20,23 and 26.

32. A third co-extruded film comprising at least one film layer comprising the third oriented film according to any one of claims 12, 15, 18, 21 and 27.

33. A third laminated film comprising at least one film layer comprising the third oriented film according to any one of claims 12, 15, 18, 21 and 27.

34. A process for forming an oriented polyethylene film comprising the steps of:

selecting the first polyethylene composition, the second polyethylene composition, the third polyethylene composition or any combination thereof;

forming a film from the polyethylene composition selected in step (a),

orienting the film formed in step (b) via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

35. A process for forming an oriented polyethylene film comprising the steps of:

selecting the first polyethylene composition, the second polyethylene composition, the third polyethylene composition or any combination thereof;

forming a film from the polyethylene composition selected in step (a),

orienting the film formed in step (b) via a simultaneous orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

36. The first oriented film according to any one of claims 1-5, 13, 16, 19, 22 and 25, wherein the first oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350 MPa.

37. The second biaxially oriented film according to any one of claims 3, 4, 5, 7 and 11, wherein the second biaxially oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350MPa.

38. The third biaxially oriented film according to any one of claims 8, 9 and 12, wherein the third biaxially oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350MPa.

AMENDED CLAIMS
received by the International Bureau on 07 August 2015 (07.08.2015).

We Claim:

1. A first oriented film comprising a first polyethylene composition which comprises:

from 20 to 50 wt% of a first linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 lower than 2 g/10min; and

from 80 to 50 wt% of a second linear low density polyethylene polymer having a density lower than 0.925 g/cc and an I_2 greater than 2 g/10min;

wherein the first polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

2. The first oriented film according to claim 1, wherein the first and/or second linear low density polyethylene polymer is produced using a Ziegler-Natta catalyst.

3. The first oriented film according to claim 1, wherein the first linear low density polyethylene polymer has a density greater than 0.930 g/cc and an I_2 lower than 1 g/10min.

4. The first oriented film according to claim 1, wherein the second linear low density polyethylene polymer has a density lower than 0.920 g/cc and an I_2 greater than 4 g/10min.

5. A second oriented film comprising a second polyethylene composition which comprises:

from 50 to 80 wt% of a third linear low density polyethylene polymer having a density greater than 0.925 g/cc and an I_2 less than 2 g/10min; and

from 50 to 20 wt% of a fourth linear low density polyethylene polymer having a density lower than 0.920 g/cc and an I_2 greater than 2 g/10min;

wherein the second polyethylene composition has an I_2 from 0.5 to 10 g/10min and a density from 0.910 to 0.940 g/cc.

6. The second oriented film according to claim 5, wherein the third linear low density polyethylene polymeris produced using a Ziegler-Natta catalyst.

7. The second oriented film according to claim 5, wherein the fourth linear low density polyethylene polymer is produced using a molecular catalyst.

8. The second oriented film according to claim 5, wherein the third linear low density polyethylene polymer has a density greater than 0.930 g/cc and an I_2 lower than 1 g/10min.

9. The second oriented film according to claim 5, wherein the fourth linear low density polyethylene polymer has a density less than 0.915 g/cc an I_2 greater than 4 g/10min.

10. A third oriented film comprising a third polyethylene composition comprising:

75 to less than 100 wt% of the first polyethylene composition according to claim 1 and/or the second polyethylene composition according to claim 6; and

greater than 0 to 25 wt% of at least one resin selected from the group consisting of linear low density polyethylene, low density polyethylene, ethylene copolymers, propylene copolymers and high density polyethylene.

11. The first oriented film according to claim 1, wherein the first polyethylene composition has an $MW_{HDF>95}$greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

12. The second oriented film according to claim 5, wherein the first polyethylene composition has an $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

13. The third oriented film according to claim 10, wherein the first polyethylene composition has an $MW_{HDF>95}$ greater than 135 kg/mol and $I_{HDF>95}$ greater than 42 kg/mol.

14. The first oriented film according to any one of claims 1-2, wherein the first oriented film is oriented below the melting point of the first polyethylenecomposition.

15. The second oriented film according to any one of claims 5-9, wherein the second oriented film is oriented below the melting point of the second polyethylenecomposition.

16. The third oriented film according to claim 10, wherein the third oriented film is oriented below the melting point of the third polyethylenecomposition.

17. The first oriented film according to any one of claims 1-4, wherein the first oriented film is a biaxially oriented film.

18. The second oriented film according to any one of claims 5-9, wherein the second oriented film is a biaxially oriented film.

19. The third oriented film according to claim 10, wherein the third oriented film is a biaxially oriented film.

20. The first biaxially oriented film according to claim 17 which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

21. The second biaxially oriented film according to claim 18 which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

22. The third biaxially oriented film according to claim 19which has been oriented via a sequential orientation process with an MD draw ratio greater than 3 and a TD draw ratio greater than 5.

23. The first biaxially oriented film according to claim 17 which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

24. The second biaxially oriented film according to claim 18which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

25. The third biaxially oriented film according to claim 19which has been oriented via a simultaneous orientation process with an MD draw ratio greater than 4 and a TD draw ratio greater than 4.

26. A first co-extruded film comprising at least one film layer comprising the first oriented film according to any one of claims 1-4, 11, and 14.

27. A first laminated film comprising at least one film layer comprising the first oriented film according to any one of claims 1-4, 11, and14.

28. A second co-extruded film comprising at least one film layer comprising the second oriented film according to any one of claims 5, 12,and15.

29. A second laminated film comprising at least one film layer comprising the second oriented film according to any one of claims 5, 12, and 15,21.

30. A third co-extruded film comprising at least one film layer comprising the third oriented film according to any one of claims 10, 13, and 16.

31. A third laminated film comprising at least one film layer comprising the third oriented film according to any one of claims 10, 13, and 16.

32. The first oriented film according to any one of claims 1-4, 11, and 14, wherein the first oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40 MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350 MPa.

33. The second oriented film according to any one of claims 5-9, wherein the second oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40 MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350 MPa.

34. The third oriented film according to any one of claims 10, 13 and 16, wherein the third oriented film exhibits one or more of the following properties:

ultimate tensile strength averaged in MD and TD, measured according to ASTM D882, greater than or equal to 40 MPa; and

2% secant modulus averaged in MD and TD, measured according to ASTM D882, greater than or equal to 350 MPa.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/074992

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/32(2006.01)i; B32B 7/08(2006.01)i

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)

B32B

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

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

CNKI, GOOGLE SCHOLARCNABS, CPRSABS, VEN: film?, membrane?, oriented, polyethylene, PE, density, melt index, biaxial+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102066466 A (EXXONMOBIL OIL CORP) 18 May 2011 (2011-05-18) see description, paragraphs [0006] to [0041]	32-33
A	CN 102066466 A (EXXONMOBIL OIL CORP) 18 May 2011 (2011-05-18) see description, paragraphs [0006] to [0041]	1-31, 34-36
A	US 2009011263 A1 (CRYOVAC INC) 08 January 2009 (2009-01-08) the whole document	1-36
A	US 2010209640 A1 (DOW GLOBAL TECHNOLOGIES INC) 19 August 2010 (2010-08-19) the whole document	1-36

☐ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 December 2014	**21 January 2015**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN) **6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China**	**XIONG,Yanbing**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62084082**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/074992

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

[1] This Authority considers that there are more inventions covered by the claims indicated as follows:

[2] I: Claims 1, 5, 10, 20-22 and 34-36 direct to the oriented films;

[3] II: Claims 26, 28 and 30 direct to the co-extruded films;

[4] III: Claims 27, 29 and 31 direct to the laminated films;

[5] IV: Claims 32 and 33 direct to the processes for forming an oriented polyethylene films.

[6] The same or corresponding technical feature of claims above is the oriented polyethylene film, and it does not make a contribution over the prior art and can not be considered as a special technical feature within the meaning of Rule 13.2 PCT. The application, hence does not meet the requirements of unity of invention as defined in Rules 13.1 PCT.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☑ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2014/074992

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102066466	A	18 May 2011	CA	2724235	A1	19 November 2009
				US	8080294	B2	20 December 2011
				CN	102066466	B	16 July 2014
				CA	2724235	C	08 January 2013
				EP	2291438	A2	09 March 2011
				US	2009286024	A1	19 November 2009
				WO	2009139957	A2	19 November 2009
				WO	2009139957	A3	15 July 2010
US	2009011263	A1	08 January 2009	WO	2007085380	A1	02 August 2007
				US	8273447	B2	25 September 2012
				CN	101374658	B	13 February 2013
				EP	1976695	A1	08 October 2008
				CN	101374658	A	25 February 2009
US	2010209640	A1	19 August 2010	JP	2009544505	A	17 December 2009
				EP	2049331	A1	22 April 2009
				CA	2658945	A1	14 February 2008
				JP	2013010353	A	17 January 2013
				TW	I435806	B	01 May 2014
				CN	101117036	A	06 February 2008
				IN	200900555	P4	05 June 2009
				WO	2008017244	A1	14 February 2008
				MX	2009002183	A	31 March 2009
				CN	101522414	A	02 September 2009
				TW	200918309	A	01 May 2009
				BRP	I0714109	A2	01 January 2013