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

AUSGERICHTETE POLYETHYLENFILME UND VERFAHREN ZUR HERSTELLUNG DAVON

FILMS DE POLYÉTHYLÈNE ORIENTÉS ET LEUR PROCÉDÉ DE FABRICATION

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(56) References cited:
CN-A- 102 066 466
US-A1- 2009 011 263
US-A1- 2009 011 263
US-A1- 2009 286 024
US-A1- 2010 209 640
US-A1- 2010 209 640

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Description

Field of Invention

[0001] The instant invention relates to oriented polyethylene films.

Background of the Invention

[0002] 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.

[0003] US2009286024A1 relates to biaxially oriented LLDPE blends.

Summary of the Invention

[0004] The instant invention includes oriented polyethylene films.

[0005] 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 or equal to 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; wherein the first oriented film is produced by a tenter frame process.

Detailed Description of the Invention

[0006] The instant invention includes oriented polyethylene films.

[0007] 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; wherein the first oriented film is produced by a tenter frame process.

[0008] 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%.

[0009] The first linear low density polyethylene polymer has a density greater than or equal to 0.925 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.

[0010] 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.

[0011] 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%.

[0012] 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.

[0013] The second linear low density polyethylene polymer has an I_2 greater than or equal to 2 g/lOmin. All individual values and subranges from 2 g/lOmin 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/lOmin. 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.

[0014] The first polyethylene composition has an I_2 from 0.5 to 10 g/lOmin. All individual values and subranges from 0.5 to 10 g/lOmin 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/lOmin 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/lOmin, or in the alternative, from 0.5 to 5 g/lOmin, or in the alternative, from 5 to 10 g/lOmin, or in the alternative, from 2 to 8 g/lOmin, or in the alternative, from 3 to 7 g/lOmin.

[0015] 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.

[0016] 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.

[0017] 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/lOmin.

[0018] 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.

[0019] 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/cc and 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), 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), 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).

[0020] 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.

[0021] 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.

[0022] 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.

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

Examples

[0028] The following examples illustrate the present invention but are not intended to limit the scope of the invention.

Polyethylene Examples 1-3

[0029] 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/lOmin;
PE Polymer 2 is anLLDPEmade usinga Ziegler-Natta catalyst and having a density 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 6211 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-lis 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/lOmin and is commercially available from The Dow Chemical Company. 0,9 mm (33-mil) cast sheets were made with a Dr. Collin cast film line (L/D = 25 and D = 30mm) equipped with a 30 cm (12 inch) wide flat die. The die gap was 1,1 mm (45 mil) and output rate was about8 kg/h.

Melt temperature was 244 °C and die temperature was set at 260 °C.

[0030] 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.

[0031] 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.

[0032] 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	Compone nt 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 6211; 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 6211	0.925	1.6	127	37.9

[0033] 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

(continued)

	Raw material	Fabrication process	Process conditions
Inventive Film 2	**PE Comp. Ex. 2**	Tenter frame biaxial orientation on aAccupull stretcher.	Simultaneously biaxial orientation. Draw ratio 4x8 Orientation temperature 120 °C

[0034] 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

[0035] 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 p 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.

[0036] 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/ 10mi n)	Reactor 2 catalyst	Reactor 2 Product density (g/cc)*	Reactor 2 Product I_2 (g/ 10mi n)	Reactor 1/Reactor 2 split, %	Final product density (g/cc)	Final Produc t 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	Molecu lar	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 6211	148	51.3
PE Comp. 5-a	90% PE Comp. 5 + 10% LDPE 6211	158	56.4
PE Comp. 5-b	85% PE Comp. 5 + 15% LDPE 6211	158	53.3
PE Comp. 6-a	90% PE Comp. 6 + 10% LDPE 6211	156	59.0
PE Comp. 6-b	85% PE Comp. 6 + 15% LDPE 6211	158	59.7
PE Comp. 7-a	90% PE Comp. 7 + 10% LDPE 6211	150	61.9
PE Comp. 7-b	85% PE Comp. 7 + 15% LDPE 6211	153	60.9

[0037] 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

(continued)

Oven temperature (°C)	110	113	115	117	120	122	125	127
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

[0038] 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

[0039] 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.

[0040] 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.

[0041] Film gloss at 20° was determined using ASTM D2457 while haze was done via ASTM D1003 and clarity by ASTM D1746.

[0042] 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 <600 kPa (<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.

[0043] The CEF column is packed with glass beads at 125 μm±6% (such as those commercially available from MO-SCI Specialty Products) with 3,2 mm (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.

[0044] 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 ($MW_{HDF\geq 95}$) and high density fraction index ($I_{HDF>95}$)

[0045] 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.

[0046] 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".

[0047] 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

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 or equal to 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
   wherein the first oriented film is produced by a tenter frame process.

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. 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.

6. 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.

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

8. The first biaxially oriented film according to claim 7 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.

9. The first biaxially oriented film according to claim 7 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.

10. A first co-extruded film comprising at least one film layer comprising the first oriented film according to any one of claims 1-4, and 5-6.

11. A first laminated film comprising at least one film layer comprising the first oriented film according to any one of claims 1-4, and 5-6.

12. The first oriented film according to any one of claims 1-4, and 5-6, 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.

Patentansprüche

1. Eine erste gereckte Folie, die eine erste Polyethylenzusammensetzung beinhaltet, die Folgendes beinhaltet:

zu 20 bis 50 Gew.-% ein erstes lineares Polyethylenpolymer niederer Dichte, das eine Dichte von mehr als 0,925 g/cm^3 und einen I_2 von weniger als 2 g/10 min aufweist; und zu 80 bis 50 Gew.-% ein zweites lineares Polyethylenpolymer niederer Dichte, das eine Dichte von weniger als oder gleich 0,925 g/cm^3 und einen I_2 von mehr als 2 g/10 min aufweist;
wobei die erste Polyethylenzusammensetzung einen I_2 von 0,5 bis 10 g/10 min und
eine Dichte von 0,910 bis 0,940 g/cm^3 aufweist,
wobei die erste gereckte Folie durch ein Spannrahmenverfahren hergestellt wird.

2. Erste gereckte Folie gemäß Anspruch 1, wobei das erste und/oder das zweite lineare Polyethylenpolymer niederer Dichte unter Verwendung eines Ziegler-Natta-Katalysators hergestellt wird.

3. Erste gereckte Folie gemäß Anspruch 1, wobei das erste lineare Polyethylenpolymer niederer Dichte eine Dichte von mehr als 0,930 g/cm^3 und einen I_2 von weniger als 1 g/10 min aufweist.

4. Erste gereckte Folie gemäß Anspruch 1, wobei das zweite lineare Polyethylenpolymer niederer Dichte eine Dichte von weniger als 0,920 g/cm^3 und einen I_2 von mehr als 4 g/10 min aufweist.

5. Erste gereckte Folie gemäß Anspruch 1, wobei die erste Polyethylenzusammensetzung ein $MW_{HDF>95}$ von mehr als 135 kg/mol und einen $I_{HDF>95}$ von mehr als 42 kg/mol aufweist.

6. Erste gereckte Folie gemäß einem der Ansprüche 1-2, wobei die erste gereckte Folie unter dem Schmelzpunkt der ersten Polyethylenzusammensetzung gereckt wird.

7. Erste gereckte Folie gemäß einem der Ansprüche 1-4, wobei die erste gereckte Folie eine biaxial gereckte Folie ist.

8. Erste biaxial gereckte Folie gemäß Anspruch 7, die über ein Verfahren der sequentiellen Reckung mit einem MD-Ziehverhältnis von mehr als 3 und einem TD-Ziehverhältnis von mehr als 5 gereckt wurde.

9. Erste biaxial gereckte Folie gemäß Anspruch 7, die über ein Verfahren der simultanen Reckung mit einem MD-Ziehverhältnis von mehr als 4 und einem TD-Ziehverhältnis von mehr als 4 gereckt wurde.

10. Eine erste koextrudierte Folie, die mindestens eine Folienschicht beinhaltet, die die erste gereckte Folie gemäß einem der Ansprüche 1-4 und 5-6 beinhaltet.

11. Eine erste laminierte Folie, die mindestens eine Folienschicht beinhaltet, die die erste gereckte Folie gemäß einem der Ansprüche 1-4 und 5-6 beinhaltet.

12. Erste gereckte Folie gemäß einem der Ansprüche 1-4 und 5-6, wobei die erste gereckte Folie eine oder mehrere der folgenden Eigenschaften vorweist:

eine Zugfestigkeit, in MD und TD gemittelt, gemessen gemäß ASTM D882, von mehr als oder gleich 40 MPa; und einen 2%-Sekantenmodul, in MD und TD gemittelt, gemessen gemäß ASTM D882, von mehr als oder gleich

350 MPa.

Revendications

1. Un premier film orienté comprenant une première composition de polyéthylène qui comprend :

   de 20 à 50 % en poids d'un premier polymère de polyéthylène basse densité linéaire ayant une masse volumique supérieure à 0,925 g/cm^3 et un I_2 inférieur à 2 g/10 min; et de 80 à 50 % en poids d'un deuxième polymère de polyéthylène basse densité linéaire ayant une masse volumique inférieure ou égale à 0,925 g/cm^3 et un I_2 supérieur à 2g/10min;
   où la première composition de polyéthylène a un I_2 allant de 0,5 à 10 g/10 min et une masse volumique allant de 0,910 à 0,940 g/cm^3
   où le premier film orienté est produit par un procédé de rame élargisseuse.

2. Le premier film orienté selon la revendication 1, où le premier et/ou deuxième polymère de polyéthylène basse densité linéaire est produit à l'aide d'un catalyseur Ziegler-Natta.

3. Le premier film orienté selon la revendication 1, où le premier polymère de polyéthylène basse densité linéaire a une masse volumique supérieure à 0,930 g/cm^3 et un I_2 inférieur à 1 g/10 min.

4. Le premier film orienté selon la revendication 1, où le deuxième polymère de polyéthylène basse densité linéaire a une masse volumique inférieure à 0,920 g/cm^3 et un I_2 supérieur à 4 g/10 min.

5. Le premier film orienté selon la revendication 1, où la première composition de polyéthylène a une $MW_{HDF>95}$ supérieure à 135 kg/mole et un $I_{HDF>95}$ supérieur à 42 kg/mole.

6. Le premier film orienté selon l'une quelconque des revendications 1 à 2, où le premier film orienté est orienté en-dessous du point de fusion de la première composition de polyéthylène.

7. Le premier film orienté selon l'une quelconque des revendications 1 à 4, où le premier film orienté est un film orienté biaxialement.

8. Le premier film orienté biaxialement selon la revendication 7 qui a été orienté par l'intermédiaire d'un procédé d'orientation séquentielle avec un rapport d'étirage SM supérieur à 3 et un rapport d'étirage ST supérieur à 5.

9. Le premier film orienté biaxialement selon la revendication 7 qui a été orienté par l'intermédiaire d'un procédé d'orientation simultanée avec un rapport d'étirage SM supérieur à 4 et un rapport d'étirage ST supérieur à 4.

10. Un premier film coextrudé comprenant au moins une couche de film comprenant le premier film orienté selon l'une quelconque des revendications 1 à 4, et 5 à 6.

11. Un premier film stratifié comprenant au moins une couche de film comprenant le premier film orienté selon l'une quelconque des revendications 1 à 4, et 5 à 6.

12. Le premier film orienté selon l'une quelconque des revendications 1 à 4, et 5 à 6, où le premier film orienté présente une ou plusieurs des propriétés suivantes :

    une résistance ultime à la traction moyennée en SM et ST, mesurée selon l'ASTM D882, supérieure ou égale à 40 MPa ; et
    un module sécant à 2 % moyenné en SM et ST, mesuré selon l'ASTM D882, supérieur ou égal à 350 MPa.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 2009286024 A1 **[0003]**
- US 5272236 A **[0019]**
- US 5278272 A **[0019]**
- US 5380810 A **[0019]**
- WO 2005090425 A **[0019]**
- WO 2005090426 A **[0019]**
- WO 2005090427 A **[0019]**
- US 20110015346 A1 **[0043]**
- US 8372931 B **[0043]**

Non-patent literature cited in the description

- **MONRABAL et al.** *Macromol. Symp.,* 2007, vol. 257, 71-79 **[0042]**
- **A. M. STRIEGEL ; W. W. YAU.** Modern Size-Exclusion Liquid Chromatography. 2009, 242-263 **[0045]**