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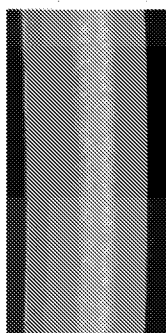
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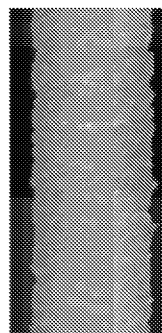
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- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

(54) Title: POLYETHYLENE BLENDS AND EXTRUDATES AND METHODS OF MAKING THE SAME



a.



b.

FIG. 1

(57) Abstract: A polymer blend including a first polyethylene and second polyethylene is provided, wherein the polymer blend has a density of 0.910 g/cm³ to 0.965 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min. The first polyethylene can include at least 80 mol% ethylene and have: a density of 0.910 g/cm³ to 0.960 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min, and the second polyethylene can include at least 80 mol% ethylene and have: a density of 0.915 g/cm³ to 0.970 g/cm³ and a melt index (I_{2.16}) of 0.01 dg/min to 10 dg/min. Polymer extrudates of the polymer blend, particularly wire- and cable-coatings, as well as methods of making the polymer extrudates are also provided.



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**POLYETHYLENE BLENDS AND EXTRUDATES AND METHODS OF MAKING
THE SAME**

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CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Serial No. 62/516,942, filed June 8, 2017, the disclosure of which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

10 [0002] The present disclosure relates to polyethylene blends and extrudates of a first polyethylene and a second polyethylene having a desirable balance of properties for use as a wire-coating and/or a cable-coating.

BACKGROUND OF THE INVENTION

15 [0003] Polyethylene compositions, particularly compositions having a narrow molecular weight distribution, can suffer from melt flow instability (*e.g.*, melt fracture, sharkskin, and stick-slip) during processing for coating applications, *e.g.*, wire and cable. Melt instability is believed to be related to the high shear rates (*e.g.*, 1,000–60,000 s⁻¹) experienced by such compositions when forming the wire-coating and/or cable-coating as a result of the of high line speeds (*e.g.*, > 600 m/min) utilized in achieving the desired thin layer of polyethylene for
20 such applications. For example, linear low density polyethylene (LLDPE) can experience a high degree of shear flow deformation as it is extruded through an annular die at high shear rates. However, in wire-coating and/or cable-coating applications, a smooth surface of the polyethylene layer is aesthetically desirable as well as functionally desirable so that the polyethylene layer can have a substantially flawless interface with a conductor layer to
25 maximize electrical properties performance. In addition, reactive processing, *e.g.*, silane grafting and/or crosslinking, also impacts the ability to efficiently and effectively process the compositions for these applications.

[0004] Thus, there is a need for polyethylene blends, which possess good processability and can be extruded at high shear rates to form extrudates, particularly a wire-coating and/or
30 a cable-coating, having a substantially smooth surface.

SUMMARY OF THE INVENTION

[0005] It has been discovered that a polymer blend having good processability, which can be extruded at higher shear rates to form extrudates with minimal melt fracture (*i.e.*, with a smooth surface) may be achieved by blending a lower density first polyethylene with a higher
35 density second polyethylene.

[0006] Disclosed herein is a polymer blend comprising a first polyethylene and a second polyethylene, wherein the polymer blend may have a density of 0.910 g/cm³ to 0.965 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min. The first polyethylene can comprise at least 80 mol% ethylene and have: a density of 0.910 g/cm³ to 0.960 g/cm³ and a melt index
5 (I_{2.16}) of 0.10 dg/10 min to 10 dg/ min. The second polyethylene can comprise at least 80 mol% ethylene and have: a density of 0.915 g/cm³ to 0.970 g/cm³ and a melt index (I_{2.16}) of 0.01 dg/min to 10 dg/ min.

[0007] In other aspects, a method for preparing a polymer extrudate is disclosed herein, wherein the polymer extrudate may have a density of 0.910 g/cm³ to 0.965 g/cm³ and a melt
10 index (I_{2.16}) of 0.10 dg/min to 10 dg/min. The method may comprise blending a first polyethylene comprising at least 80 mol% ethylene and having: a density of 0.910 g/cm³ to 0.96 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/10 min to 10 dg/ min with a second polyethylene comprising at least 80 mol% ethylene and having: a density of 0.915 g/cm³ to 0.970 g/cm³ and a melt index (I_{2.16}) of 0.01 dg/min to 10 dg/ min.

15 [0008] Additionally disclosed are extrudates comprising a polymer blend as described herein and/or produced according to a method as described herein.

BRIEF DESCRIPTION OF THE FIGURES

[0009] The drawings described herein are for illustrative purposes only of selected embodiments and not all possible implementations, and are not intended to limit the scope of
20 the present disclosure.

[0010] FIGS. 1a and 1b are optical microscopy photographs of Sample 1 and Comparative Sample 1, respectively.

[0011] FIGS. 2a and 2b are optical microscopy photographs of Sample 1 and Comparative Sample 2, respectively.

25 [0012] FIGS. 3a and 3b are optical microscopy photographs of Sample 1 and Comparative Sample 3, respectively.

[0013] FIGS. 4a and 4b are optical microscopy photographs of Sample 1 and Comparative Sample 4, respectively.

[0014] FIGS. 5a and 5b are optical microscopy photographs of Sample 1 and
30 Comparative Sample 5, respectively.

[0015] FIGS. 6a and 6b are optical microscopy photographs of Sample 1 and Comparative Sample 6, respectively.

[0016] FIGS. 7a and 7b are optical microscopy photographs of Sample 1 and Comparative Sample 7, respectively.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Before the present polymers, compounds, components, compositions, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated this invention is not limited to specific polymers, compounds, components, compositions, reactants, reaction conditions, ligands, metallocene structures, or the like, as such may vary, unless otherwise specified. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[0018] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless otherwise specified.

10 **Definitions & Measurement Techniques**

[0019] For the purposes of this disclosure, the following definitions will apply, unless otherwise stated.

[0020] Molecular weight distribution ("MWD") is equivalent to the expression M_w/M_n . The expression M_w/M_n is the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n). The weight average molecular weight is given by

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

the number average molecular weight is given by

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

the z-average molecular weight is given by

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$$M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

where n_i in the foregoing equations is the number fraction of molecules of molecular weight M_i . Unless indicated otherwise, measurements of M_w , M_z , and M_n are determined by Gel Permeation Chromatography. The measurements proceed as follows. Gel Permeation Chromatography (Agilent PL-220), equipped with three in-line detectors, a differential refractive index detector (DRI), a light scattering (LS) detector, and a viscometer, is used.

Experimental details, including detector calibration, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Vol. 34, No. 19, pp. 6812-6820, (2001). Three Agilent PLgel 10 μ m Mixed-B LS columns are used. The nominal flow rate is 0.5 mL/min, and the nominal injection volume is 300 μ L. The various transfer lines, columns, viscometer and differential refractometer (the DRI detector) are contained in an oven maintained at 145°C. Solvent for the experiment is prepared by dissolving 6 grams of butylated hydroxytoluene as an antioxidant in 4 liters of Aldrich reagent grade 1,2,4-trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.1 μ m Teflon filter. The TCB is then degassed with an online degasser before entering the GPC-3D. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160°C with continuous shaking for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at about 21°C and 1.284 g/ml at 145°C. The injection concentration is from 0.5 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample, the DRI detector and the viscometer are purged. The flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8 hours before injecting the first sample. The LS laser is turned on at least 1 to 1.5 hours before running the samples. The concentration, *c*, at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, *I*_{DRI}, using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc),$$

where *K*_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, *n* = 1.500 for TCB at 145°C and λ = 690 nm. Units on parameters throughout this description of the GPC-3D method are such that concentration is expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g.

[0021] The LS detector is a Wyatt Technology High Temperature DAWN HELEOS. The molecular weight, *M*, at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, *LIGHT SCATTERING FROM POLYMER SOLUTIONS*, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c.$$

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , *c* is the polymer concentration determined from the DRI analysis, *A*₂ is the second virial coefficient.

$P(\theta)$ is the form factor for a monodisperse random coil, and K_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system, which take the same value as the one obtained from DRI method. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 657 \text{ nm}$.

[0022] A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2,$$

where c is concentration and was determined from the DRI output.

[0023] Alternatively, polymer molecular weight (M_n , M_w , M_z) and molecular weight distribution (M_w/M_n) are determined using Size-Exclusion Chromatography (SEC). Equipment consists of a High Temperature Size Exclusion Chromatograph (either from Waters Corporation or Polymer Laboratories), with a differential refractive index detector (DRI) or infrared (IR) detector. In the examples and specification herein, DRI was used, and mono-dispersed polystyrene is the standard with Mark-Howink ("MH") constants of $\alpha=0.6700$, and $K=0.000175$. Three Polymer Laboratories PLgel 10mm Mixed-B columns are used. The nominal flow rate is $0.5 \text{ cm}^3/\text{min}$ and the nominal injection volume is $300 \mu\text{L}$. The various transfer lines, columns and differential refractometer (the DRI detector) are contained in an oven maintained at $135\text{-}145^\circ\text{C}$, and a dissolution temperature of 160°C . Solvent is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of reagent grade 1,2,4-trichlorobenzene (TCB), the final concentration of polymer is from 0.4 to 0.7 mg/mL . The TCB mixture is then filtered through a $0.7 \mu\text{m}$ glass pre-filter and subsequently through a $0.1 \mu\text{m}$ Teflon filter. The TCB is then degassed with an online degasser before entering the column. The MH constants were as follows: $K=0.000579$, $\alpha=0.695$ (DRI); and $K=0.0002290$, $\alpha=0.7050$, (IR). Values for M_n are $\pm 2,000 \text{ g/mole}$, for M_w are $\pm 5,000 \text{ g/mole}$, and M_z are $\pm 50,000 \text{ g/mole}$.

[0024] Unless indicated otherwise, the branching index (g'_{vis}) is calculated using the output of the GPC-DRI-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i},$$

5 where the summations are over the chromatographic slices, i , between the integration limits.

[0025] The branching index g'_{vis} is defined as:

$$g'_{vis} = \frac{[\eta]_{avg}}{kM_v^\alpha},$$

M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. Z average branching index (g'_{Zave}) is calculated using C_i = polymer concentration in the slice i in the polymer peak times the mass of the slice squared, M_i^2 . All molecular weights are weight average unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted. This method is the preferred method of measurement and used in the examples and throughout the disclosures unless otherwise specified. *See also, for background*, Macromolecules, Vol. 34, No. 19, Effect of Short Chain Branching on the Coil Dimensions of Polyolefins in Dilute Solution, Sun *et al.*, pg. 6812-6820 (2001).

[0026] Unless indicated otherwise, the melt strength of the polymers described herein at a particular temperature may be determined with a Gottfert Rheotens Melt Strength Apparatus. To determine the melt strength, unless otherwise stated, a polymer melt strand extruded from the capillary die is gripped between two counter-rotating wheels on the apparatus. The take-up speed is increased at a constant acceleration of 2.4 mm/sec². The maximum pulling force (in the unit of cN) achieved before the strand breaks or starts to show draw-resonance is determined as the melt strength. The temperature of the rheometer is set at 190°C. The capillary die has a length of 30 mm and a diameter of 2 mm. The polymer melt is extruded from the die at a speed of 10 mm/sec. The distance between the die exit and the wheel contact point should be 122 mm.

[0027] Unless indicated otherwise, the density of the polymers described herein may be determined using chips cut from plaques compression molded in accordance with ASTM D-1928 Procedure C, aged in accordance with ASTM D-618 Procedure A, and measured as specified by ASTM D-1505.

[0028] The melt index (MI) ($I_{2.16}$ or simply I_2 for shorthand) of the polymers described herein may be determined according to ASTM D1238, condition E (190°C/2.16 kg) reported in decigrams per minute (dg/min).

Polymer Blends

5 [0029] Typically, when polyethylene, particularly LLDPE, is extruded at higher shear rates, the polyethylene experiences shear flow deformation and undergoes various forms of melt fracture instabilities (e.g., sharkskin, stick-slip, gross melt fracture) resulting in an undesirably rough extrudate surface. However, it was unexpectedly discovered that polymer
10 blends having improved processability, which can be extruded at higher shear rates to produce extrudates having a substantially smooth surface with minimal melt fracture, can be achieved by blending a lower density first polyethylene with a higher density second polyethylene. In particular, a polymer blend comprising a first polyethylene and a second polyethylene is provided herein, wherein the polymer blend has a density of 0.910 g/cm³ to 0.965 g/cm³ and a melt index ($I_{2.16}$) of 0.10 dg/min to 10 dg/min.

15 First Polyethylene

[0030] The polymer blend can include at least a first polyethylene. The first polyethylene for use in the polymer blend may comprise from 70.0 mol% to 100.0 mol% of units derived from ethylene. The lower limit on the range of ethylene content may be 70.0 mol%, 75.0 mol%, 80.0 mol%, 85.0 mol%, 90.0 mol%, 92.0 mol%, 94.0 mol%, 95.0 mol%, 96.0 mol%,
20 97.0 mol%, 98.0 mol%, or 99.0 mol% based on the mol% of polymer units derived from ethylene. The first polyethylene may have an upper ethylene limit of 80.0 mol%, 85.0 mol%, 90.0 mol%, 92.0 mol%, 94.0 mol%, 95.0 mol%, 96.0 mol%, 97.0 mol%, 98.0 mol%, 99.0 mol%, 99.5 mol%, or 100.0 mol%, based on polymer units derived from ethylene. For polyethylene copolymers, the first polyethylene may have less than 50.0 mol% of polymer
25 units derived from one or more C₃-C₂₀ olefin comonomers, preferably C₃ to C₁₀ α -olefins, and more preferably C₄ to C₈ α -olefins. The α -olefin comonomer may be linear, branched, cyclic and/or substituted, and two or more comonomers may be used, if desired. Examples of suitable comonomers include propylene, butene, 1-pentene; 1-pentene with one or more methyl, ethyl, or propyl substituents; 1-hexene; 1-hexene with one or more methyl, ethyl, or
30 propyl substituents; 1-heptene; 1-heptene with one or more methyl, ethyl, or propyl substituents; 1-octene; 1-octene with one or more methyl, ethyl, or propyl substituents; 1-nonene; 1-nonene with one or more methyl, ethyl, or propyl substituents; ethyl, methyl, or dimethyl-substituted 1-decene; 1-dodecene; and styrene. Particularly suitable comonomers include 1-butene, 1-hexene, and 1-octene, 1-hexene, and mixtures thereof, preferably, an

alpha-olefin, *e.g.*, hexene or octene. The lower limit on the range of C₃-C₂₀ olefin-content may be 25.0 mol%, 20.0 mol%, 15.0 mol%, 10.0 mol%, 8.0 mol%, 6.0 mol%, 5.0 mol%, 4.0 mol%, 3.0 mol%, 2.0 mol%, 1.0 mol%, or 0.5 mol%, based on polymer units derived from the C₃-C₂₀ olefin. The upper limit on the range of C₃-C₂₀ olefin-content may be 20.0 mol%,
 5 15.0 mol%, 10.0 mol%, 8.0 mol%, 6.0 mol%, 5.0 mol%, 4.0 mol%, 3.0 mol%, 2.0 mol%, or 1.0 mol%, based on polymer units derived from the C₃ to C₂₀ olefin. Any of the lower limits may be combined with any of the upper limits to form a range. Comonomer content is based on the total content of all monomers in the polymer.

[0031] In various aspects, the first polyethylene may comprise from about 8 wt% to about
 10 15 wt%, of C₃-C₁₀ α -olefin derived units, and from about 92 wt% to about 85 wt% ethylene derived units, based upon the total weight of the polymer.

[0032] In another embodiment, the first polyethylene comprises from about 9 wt% to about 12 wt%, of C₃-C₁₀ α -olefin derived units, and from about 91 wt% to about 88 wt% ethylene derived units, based upon the total weight of the polymer.

[0033] The first polyethylene may have a melt index (MI) (I_{2.16} or simply I₂ for shorthand) according to ASTM D1238, condition E (190°C/2.16 kg) reported in decigrams per minute (dg/min), of $\geq$ about 0.050 dg/min, *e.g.*, $\geq$ about 0.10 dg/min, $\geq$ about 0.15 dg/min, $\geq$ about 0.25 dg/min, $\geq$ about 0.50 dg/min, $\geq$ about 0.75 dg/min, $\geq$ about 1.0 dg/min, $\geq$ about 2.0 dg/min, $\geq$ about 3.0 dg/min, $\geq$ about 4.0 dg/min, $\geq$ about 5.0 dg/min, $\geq$ about 6.0
 20 dg/min, $\geq$ about 7.0 dg/min, $\geq$ about 8.0 dg/min, $\geq$ about 9.0 dg/min, $\geq$ about 10 dg/min, or $\geq$ about 12 dg/min. Additionally, the first polyethylene may have a melt index (I_{2.16}) $\leq$ about 12 dg/min, $\leq$ about 10 dg/min, $\leq$ about 9.0 dg/min, $\leq$ about 8.0 dg/min, $\leq$ about 7.0 dg/min, $\leq$ about 6.0 dg/min, $\leq$ about 5.0 dg/min, $\leq$ about 4.0 dg/min, $\leq$ about 3.0 dg/min, $\leq$ about 2.0 dg/min, $\leq$ about 1.0 dg/min, $\leq$ about 0.75 dg/min, $\leq$ about 0.50 dg/min, $\leq$ about 0.25 dg/min,
 25 $\leq$ about 0.15 dg/min or $\leq$ about 0.10 dg/min. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 0.050 to about 12 dg/min, about 0.25 to about 5.0 dg/min, about 0.50 to about 8.0 dg/min, *etc.* In particular, the first polyethylene may have a melt index (I_{2.16}) of about 0.10 dg/min to about 10 dg/min.

[0034] The first polyethylene may also have a High Load Melt Index (HLMI) (I_{21.6}) measured in accordance with ASTM D-1238, condition F (190°C/21.6 kg). For a given polymer having a Melt Index (MI) and Melt Index Ratio (MIR) as defined herein, the HLMI is fixed and can be calculated in accordance with the following paragraph.

[0035] The first polyethylene may have a MIR or $I_{21.6}/I_{2.16}$ from 25 to 80, alternatively, from 25 to 60, alternatively, from about 30 to about 55, and alternatively, from about 35 to about 50.

[0036] The first polyethylene may have a density $\geq$ about 0.905 g/cm³, $\geq$ about 0.910 g/cm³, $\geq$ about 0.912 g/cm³, $\geq$ about 0.914 g/cm³, $\geq$ about 0.916 g/cm³, $\geq$ about 0.918 g/cm³, $\geq$ about 0.920 g/cm³, $\geq$ about 0.925 g/cm³, $\geq$ about 0.930 g/cm³, $\geq$ about 0.935 g/cm³, $\geq$ about 0.940 g/cm³, $\geq$ about 0.945 g/cm³, $\geq$ about 0.950 g/cm³, $\geq$ about 0.955 g/cm³, $\geq$ about 0.960 g/cm³, or $\geq$ about 0.965 g/cm³. Additionally or alternatively, first polyethylene may have a density $\leq$ about 0.965 g/cm³, *e.g.*, $\leq$ about 0.960 g/cm³, $\leq$ about 0.955 g/cm³, $\leq$ about 0.950 g/cm³, $\leq$ about 0.945 g/cm³, $\leq$ about 0.940 g/cm³, $\leq$ about 0.935 g/cm³, $\leq$ about 0.930 g/cm³, $\leq$ about 0.925 g/cm³, $\leq$ about 0.920 g/cm³, or $\leq$ about 0.918 g/cm³. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations any of the above-enumerated values, *e.g.*, from about 0.905 to about 0.965 g/cm³, about 0.910 to about 0.960 g/cm³, about 0.916 to about 0.950 g/cm³, about 0.918 to about 0.945 g/cm³, *etc.* In particular, the first polyethylene may have a density from about 0.910 to about 0.960 g/cm³.

[0037] Typically, although not necessarily, the first polyethylene may have a molecular weight distribution (MWD, defined as M_w/M_n) of about 1.5 to about 8.5, about 2.0 to about 6.0, about 2.5 to about 5.5, or about 3.0 to about 4.0. In particular, the first polyethylene may have a molecular weight distribution (M_w/M_n) of about 2.0 to 6.0.

[0038] The weight average molecular weight (M_w) of the first polyethylene may be in the range of about 50 g/mol to about 250,000 g/mol, about 100 g/mol to about 100,000 g/mol, preferably about 100 g/mol to about 150 g/mol.

[0039] The melt strength of the first polyethylene may be in the range from about 1 to about 100 cN, about 1 to about 50 cN, about 1 to about 25 cN, about 3 to about 15 cN, about 4 to about 12 cN, or about 5 to about 10 cN.

[0040] The first polyethylene may also be characterized by an averaged 1% secant modulus (M) of 10,000 to 60,000 psi (pounds per square inch), alternatively, from 20,000 to 40,000 psi, alternatively, from 20,000 to 35,000 psi, alternatively, from 25,000 to 35,000 psi, and alternatively, from 28,000 to 33,000 psi, and a relation between M and the dart drop impact strength in g/mil (DIS) complying with formula (A):

$$DIS \geq 0.8 * [100 + e^{(11.71 - 0.000268M + 2.183 \times 10^{-9} M^2)}] \quad (A),$$

where “e” represents 2.7183, the base Napierian logarithm, M is the averaged modulus in psi, and DIS is the 26 inch dart impact strength. The DIS is preferably from about 120 to about 1000 g/mil, even more preferably, from about 150 to about 800 g/mil.

[0041] Typically, the first polyethylene useful herein tends to be highly linear as evidenced by a high branching index. Thus, in any embodiment the first polyethylene may have a g'vis of 0.85 to 0.99, particularly, 0.87 to 0.97, 0.89 to 0.97, 0.91 to 0.97, 0.93 to 0.95, or 0.97 to 0.99. In various aspects, the first polyethylene may be considered a LLDPE.

[0042] The first polyethylene may be made by any suitable polymerization method including solution polymerization, slurry polymerization, supercritical, and gas phase polymerization using supported or unsupported catalyst systems, such as a system incorporating a metallocene catalyst.

[0043] As used herein, the term “metallocene catalyst” is defined to comprise at least one transition metal compound containing one or more substituted or unsubstituted cyclopentadienyl moiety (Cp) (typically two Cp moieties) in combination with a Group 4, 5, or 6 transition metal, such as, zirconium, hafnium, and titanium.

[0044] Metallocene catalysts generally require activation with a suitable co-catalyst, or activator, in order to yield an “active metallocene catalyst”, i.e., an organometallic complex with a vacant coordination site that can coordinate, insert, and polymerize olefins. Active catalyst systems generally include not only the metallocene complex, but also an activator, such as an alumoxane or a derivative thereof (preferably methyl alumoxane), an ionizing activator, a Lewis acid, or a combination thereof. Alkylalumoxanes (typically methyl alumoxane and modified methylalumoxanes) are particularly suitable as catalyst activators. The catalyst system may be supported on a carrier, typically an inorganic oxide or chloride or a resinous material such as, for example, polyethylene or silica.

[0045] Zirconium transition metal metallocene-type catalyst systems are particularly suitable. Non-limiting examples of metallocene catalysts and catalyst systems useful in practicing the present invention include those described in, U.S. Patent Nos. 5,466,649, 6,476,171, 6,225,426, and 7,951,873, and in the references cited therein, all of which are fully incorporated herein by reference. Particularly useful catalyst systems include supported dimethylsilyl bis(tetrahydroindenyl) zirconium dichloride.

[0046] Supported polymerization catalyst may be deposited on, bonded to, contacted with, or incorporated within, adsorbed or absorbed in, or on, a support or carrier. In another embodiment, the metallocene is introduced onto a support by slurrying a pre-supported activator in oil, a hydrocarbon such as pentane, solvent, or non-solvent, then adding the

metallocene as a solid while stirring. The metallocene may be finely divided solids. Although the metallocene is typically of very low solubility in the diluting medium, it is found to distribute onto the support and be active for polymerization. Very low solubilizing media such as mineral oil (e.g., Kaydo™ or Drakol™) or pentane may be used. The diluent
5 can be filtered off and the remaining solid shows polymerization capability much as would be expected if the catalyst had been prepared by traditional methods such as contacting the catalyst with methylalumoxane in toluene, contacting with the support, followed by removal of the solvent. If the diluent is volatile, such as pentane, it may be removed under vacuum or by nitrogen purge to afford an active catalyst. The mixing time may be greater than 4 hours,
10 but shorter times are suitable.

[0047] Typically in a gas phase polymerization process, a continuous cycle is employed where in one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed in another part of the cycle by a cooling system external to the reactor. (See *e.g.*,
15 U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661, and 5,668,228.) To obtain the first additional polyethylene polymers, individual flow rates of ethylene, comonomer, and hydrogen should be controlled and adjusted to obtain the desired polymer properties.

[0048] Suitable commercial polymers for the first polyethylene are available from
20 ExxonMobil Chemical Company as Enable™ metallocene polyethylene (mPE) resins.

[0049] In various aspects, the first polyethylene may be present in the polymer blend in an amount of about 50 wt% to about 99 wt%, about 50 wt% to about 90 wt%, or about 60 wt% to about 80 wt%, based on the total weight of the polymer blend.

Second Polyethylene

25 [0050] The polymer blend can also include a second polyethylene. The second polyethylene for use in the polymer blend may comprise from 70.0 mol% to 100.0 mol% of polymer units derived from ethylene. The lower limit on the range of ethylene content may be 70.0 mol%, 75.0 mol%, 80.0 mol%, 85.0 mol%, 90.0 mol%, 92.0 mol%, 94.0 mol%, 95.0 mol%, 96.0 mol%, 97.0 mol%, 98.0 mol%, or 99.0 mol% based on the mol% of polymer
30 units derived from ethylene. The first polyethylene may have an upper ethylene limit of 80.0 mol%, 85.0 mol%, 90.0 mol%, 92.0 mol%, 94.0 mol%, 95.0 mol%, 96.0 mol%, 97.0 mol%, 98.0 mol%, 99.0 mol%, 99.5 mol%, or 100.0 mol%, based on polymer units derived from ethylene. For polyethylene copolymers, the second polyethylene may have less than 50.0 mol% of polymer units derived from one or more C₃-C₂₀ olefin comonomers, preferably C₃ to

C₁₀ α -olefins, and more preferably C₄ to C₈ α -olefins. The α -olefin comonomer may be linear, branched, cyclic and/or substituted, and two or more comonomers may be used, if desired. Examples of suitable comonomers include propylene, butene, 1-pentene; 1-pentene with one or more methyl, ethyl, or propyl substituents; 1-hexene; 1-hexene with one or more methyl, ethyl, or propyl substituents; 1-heptene; 1-heptene with one or more methyl, ethyl, or propyl substituents; 1-octene; 1-octene with one or more methyl, ethyl, or propyl substituents; 1-nonene; 1-nonene with one or more methyl, ethyl, or propyl substituents; ethyl, methyl, or dimethyl-substituted 1-decene; 1-dodecene; and styrene. Particularly suitable comonomers include 1-butene, 1-hexene, and 1-octene, 1-hexene, and mixtures thereof, preferably, an alpha-olefin, *e.g.*, hexene or octene. The lower limit on the range of C₃-C₂₀ olefin-content may be 25.0 mol%, 20.0 mol%, 15.0 mol%, 10.0 mol%, 8.0 mol%, 6.0 mol%, 5.0 mol%, 4.0 mol%, 3.0 mol%, 2.0 mol%, 1.0 mol%, or 0.5 mol%, based on polymer units derived from the C₃-C₂₀ olefin. The upper limit on the range of C₃-C₂₀ olefin-content may be 20.0 mol%, 15.0 mol%, 10.0 mol%, 8.0 mol%, 6.0 mol%, 5.0 mol%, 4.0 mol%, 3.0 mol%, 2.0 mol%, or 1.0 mol%, based on polymer units derived from the C₃ to C₂₀ olefin. Any of the lower limits may be combined with any of the upper limits to form a range. Comonomer content is based on the total content of all monomers in the polymer.

[0051] The second polyethylene may have a MI (I_{2.16}) according to ASTM D1238, condition E (190°C/2.16 kg) reported in decigrams per minute (dg/min), of $\geq$ about 0.0050 dg/min, *e.g.*, $\geq$ about 0.0075 dg/min, $\geq$ about 0.010 dg/min, $\geq$ about 0.025 dg/min, $\geq$ about 0.050 dg/min, $\geq$ about 0.075 dg/min, $\geq$ about 0.10 dg/min, $\geq$ about 0.15 dg/min, $\geq$ about 0.25 dg/min, $\geq$ about 0.50 dg/min, $\geq$ about 0.75 dg/min, $\geq$ about 1.0 dg/min, $\geq$ about 2.0 dg/min, $\geq$ about 3.0 dg/min, $\geq$ about 4.0 dg/min, $\geq$ about 5.0 dg/min, $\geq$ about 6.0 dg/min, $\geq$ about 7.0 dg/min, $\geq$ about 8.0 dg/min, $\geq$ about 9.0 dg/min, $\geq$ about 10 dg/min, or $\geq$ about 12 dg/min. Additionally, the second polyethylene may have a melt index (I_{2.16}) $\leq$ about 12 dg/min, $\leq$ about 10 dg/min, $\leq$ about 9.0 dg/min, $\leq$ about 8.0 dg/min, $\leq$ about 7.0 dg/min, $\leq$ about 6.0 dg/min, $\leq$ about 5.0 dg/min, $\leq$ about 4.0 dg/min, $\leq$ about 3.0 dg/min, $\leq$ about 2.0 dg/min, $\leq$ about 1.0 dg/min, $\leq$ about 0.75 dg/min, $\leq$ about 0.50 dg/min, $\leq$ about 0.25 dg/min, $\leq$ about 0.15 dg/min, $\leq$ about 0.10 dg/min, $\leq$ about 0.075 dg/min, $\leq$ about 0.050 dg/min, $\leq$ about 0.025 dg/min, $\leq$ about 0.010 dg/min, or $\leq$ about 0.0075 dg/min. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 0.0050 to about 12 dg/min, about 0.0075 to about 5.0 dg/min, about 0.010 to about 1.0 dg/min, *etc.* In particular, the second polyethylene may have a melt index (I_{2.16}) of from about 0.010 dg/min to about 10 dg/min.

[0052] The second polyethylene may also have HLMI ($I_{21.6}$ or I_{21} for shorthand) measured in accordance with ASTM D-1238, condition F (190°C/21.6 kg) of $\geq$ about 1.0 dg/min, $\geq$ about 5.0 dg/min, $\geq$ about 10 dg/min, $\geq$ about 15 dg/min, $\geq$ about 20 dg/min, $\geq$ about 25 dg/min, $\geq$ about 30 dg/min, $\geq$ about 35 dg/min, $\geq$ about 40 dg/min, $\geq$ about 45 dg/min, $\geq$ about 50 dg/min, $\geq$ about 55 dg/min, $\geq$ about 60 dg/min, $\geq$ about 65 dg/min, or $\geq$ about 70 dg/min. Additionally, the second polyethylene may have a melt index ($I_{2.16}$) $\leq$ about 70 dg/min, $\leq$ about 65 dg/min, $\leq$ about 60 dg/min, $\leq$ about 55 dg/min, $\leq$ about 50 dg/min, $\leq$ about 45 dg/min, $\leq$ about 40 dg/min, $\leq$ about 35 dg/min, $\leq$ about 30 dg/min, $\leq$ about 25 dg/min, $\leq$ about 20 dg/min, $\leq$ about 15 dg/min, $\leq$ about 10 dg/min, or $\leq$ about 5.0 dg/min.

10 Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 1.0 to about 70 dg/min, about 2.0 to about 55 dg/min, about 25 to about 65 dg/min, *etc.* In particular, the second polyethylene may have an HLMI ($I_{21.6}$) of about 1.0 dg/min to about 60 dg/min.

[0053] The second polyethylene may have a MIR or $I_{21.6}/I_{2.16}$ from 50 to 2500, alternatively, from 70 to 200.

[0054] The second polyethylene may have a density $\geq$ about 0.910 g/cm³, $\geq$ about 0.915 g/cm³, $\geq$ about 0.920 g/cm³, $\geq$ about 0.925 g/cm³, $\geq$ about 0.930 g/cm³, $\geq$ about 0.935 g/cm³, $\geq$ about 0.940 g/cm³, $\geq$ about 0.945 g/cm³, $\geq$ about 0.950 g/cm³, $\geq$ about 0.955 g/cm³, $\geq$ about 0.960 g/cm³, $\geq$ about 0.965 g/cm³, $\geq$ about 0.970 g/cm³, $\geq$ about 0.975 g/cm³, or $\geq$ about 0.980 g/cm³.

20 Additionally or alternatively, second polyethylene may have a density $\leq$ about 0.980 g/cm³, *e.g.*, $\leq$ about 0.975 g/cm³, $\leq$ about 0.970 g/cm³, $\leq$ about 0.965 g/cm³, $\leq$ about 0.960 g/cm³, $\leq$ about 0.955 g/cm³, $\leq$ about 0.950 g/cm³, $\leq$ about 0.945 g/cm³, $\leq$ about 0.940 g/cm³, $\leq$ about 0.935 g/cm³, $\leq$ about 0.930 g/cm³, $\leq$ about 0.925 g/cm³, or $\leq$ about 0.920 g/cm³.

Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 0.910 to about 0.980 g/cm³, about 0.915 to about 0.975 g/cm³, about 0.920 to about 0.970 g/cm³, about 0.925 to about 0.965 g/cm³, *etc.* In particular, the second polyethylene may have a density from about 0.915 to about 0.970 g/cm³. In various aspects, the second polyethylene may be considered a medium density polyethylene (MDPE) and/or a high density polyethylene (HDPE).

30 [0055] Typically, although not necessarily, the second polyethylene may have a molecular weight distribution (MWD, defined as M_w/M_n) of about 5.0 to about 40, about 7.0 to about 30, or about 7.0 to about 20. In particular, the second polyethylene may have a molecular weight distribution (M_w/M_n) of about 7.0 to 30.

[0056] The weight average molecular weight of the second polyethylene may be in the range from about 100 g/mol to about 750 g/mol, about 150 g/mol to about 500 g/mol, preferably about 250 g/mol to about 350 g/mol.

[0057] The melt strength of the second polyethylene may be in the range from about 1 to about 100 cN, about 1 to about 50 cN, about 1 to about 25 cN, about 3 to about 15 cN, about 4 to about 12 cN, or about 5 to about 10 cN.

[0058] The second polyethylene may also have a flexural modulus, as measured according to ASTM D790, from about 500 MPa to about 2500 MPa, about 500 MPa to about 2000 MPa or about 500 MPa to about 1500 MPa.

10 [0059] Typically, the second polyethylene useful herein tends to be highly linear as evidenced by a high branching index. Thus, in any embodiment the second polyethylene may have a g'vis of 0.85 to 0.99, particularly, 0.87 to 0.97, 0.89 to 0.97, 0.91 to 0.97, 0.93 to 0.95, or 0.97 to 0.99.

[0060] The second polyethylene may be made by any suitable polymerization method including solution polymerization, slurry polymerization, supercritical, and gas phase polymerization using supported or unsupported catalyst systems, such as Ziegler-Natta-type catalysts, chromium catalysts, metallocene-type catalysts as described herein, other appropriate catalyst systems or combinations thereof, or by free-radical polymerization. In various aspects, the second polyethylene may be made by the catalysts, activators and processes described in U.S. Patent Nos. 6,342,566, 6,384,142, WO 03/040201, WO 97/19991 and U.S. Patent No. 5,741,563. Such catalysts are well known in the art, and are described in, for example, ZIEGLER CATALYSTS (Gerhard Fink, Rolf Mülhaupt and Hans H. Brintzinger, eds., Springer-Verlag 1995); Resconi et al.; and I, II METALLOCENE-BASED POLYOLEFINS (Wiley & Sons 2000). In other aspects, the second polyethylene may be produced using chrome based catalysts, such as, for example, in U.S. Patent No. 7,491,776 including that fluorocarbon does not have to be used in the production.

[0061] Suitable commercial polymers for the second polyethylene are available from ExxonMobil Chemical Company as Paxon™ grades of polyethylene, ExxonMobil™ HDPE HMA, HPA, HYA and HTA product series, *e.g.* HPA 020, HTA 001HD, HYA 600, HTA 002, HTA 108, Novapol HB-W555-A (commercially available from Nova), Marlex C513UV (commercially available from Chevron Phillips Chemical Company LP), and K54-05 Polyethylene Copolymer (commercially available from Ineos).

[0062] In various aspects, the second polyethylene may be present in the polymer blend in an amount of about 1.0 wt% to about 50 wt%, about 10 wt% to about 50 wt%, or about 20 wt% to about 40 wt%, based on the total weight of the polymer blend.

[0063] In a particular embodiment, the first polyethylene may be present in an amount of about 50 wt% to about 99 wt%, based on the total weight of the polymer blend, and the second polyethylene may be present in an amount of about 1.0 wt% to about 50 wt%, based on the total weight of the polymer blend. In another embodiment, the first polyethylene may be present in an amount of about 60 wt% to about 80 wt%, based on the total weight of the polymer blend, and the second polyethylene may be present in an amount of about 20 wt% to about 40 wt%, based on the total weight of the polymer blend.

Polymer Blend Properties

[0064] The polymer blends described herein have many advantages, such as desirable density and melt index as well as the ability to be extruded under higher shear rates while still producing extrudates having a substantially smooth surface. Thus, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a density of $\geq$ about 0.905 g/cm³, $\geq$ about 0.910 g/cm³, $\geq$ about 0.912 g/cm³, $\geq$ about 0.914 g/cm³, $\geq$ about 0.916 g/cm³, $\geq$ about 0.918 g/cm³, $\geq$ about 0.920 g/cm³, $\geq$ about 0.925 g/cm³, $\geq$ about 0.930 g/cm³, $\geq$ about 0.935 g/cm³, $\geq$ about 0.940 g/cm³, $\geq$ about 0.945 g/cm³, $\geq$ about 0.950 g/cm³, $\geq$ about 0.955 g/cm³, $\geq$ about 0.960 g/cm³, $\geq$ about 0.965 g/cm³, or $\geq$ about 0.970 g/cm³. Additionally or alternatively, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a density $\leq$ about 0.970 g/cm³, *e.g.*, $\leq$ about 0.965 g/cm³, $\leq$ about 0.960 g/cm³, $\leq$ about 0.955 g/cm³, $\leq$ about 0.950 g/cm³, $\leq$ about 0.945 g/cm³, $\leq$ about 0.940 g/cm³, $\leq$ about 0.935 g/cm³, $\leq$ about 0.930 g/cm³, $\leq$ about 0.925 g/cm³, $\leq$ about 0.920 g/cm³, or $\leq$ about 0.918 g/cm³. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 0.905 to about 0.970 g/cm³, about 0.910 to about 0.965 g/cm³, about 0.916 to about 0.950 g/cm³, about 0.918 to about 0.945 g/cm³, *etc.* In particular, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a density from about 0.910 to about 0.965 g/cm³.

[0065] Additionally or alternatively, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a melt index (I_{2.16}) according to ASTM D1238, condition E (190°C/2.16 kg) reported in decigrams per minute (dg/min), of $\geq$ about 0.050 dg/min, *e.g.*, $\geq$ about 0.10 dg/min, $\geq$ about 0.15 dg/min, $\geq$ about 0.25 dg/min, $\geq$ about 0.50 dg/min, $\geq$ about 0.75 dg/min, $\geq$ about 1.0 dg/min, $\geq$ about

2.0 dg/min, $\geq$ about 3.0 dg/min, $\geq$ about 4.0 dg/min, $\geq$ about 5.0 dg/min, $\geq$ about 6.0 dg/min, $\geq$ about 7.0 dg/min, $\geq$ about 8.0 dg/min, $\geq$ about 9.0 dg/min, $\geq$ about 10 dg/min, or $\geq$ about 12 dg/min. Additionally, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a melt index (I_{2.16}) $\leq$ about 12 dg/min, $\leq$ about 10 dg/min, $\leq$ about 9.0 dg/min, $\leq$ about 8.0 dg/min, $\leq$ about 7.0 dg/min, $\leq$ about 6.0 dg/min, $\leq$ about 5.0 dg/min, $\leq$ about 4.0 dg/min, $\leq$ about 3.0 dg/min, $\leq$ about 2.0 dg/min, $\leq$ about 1.0 dg/min, $\leq$ about 0.75 dg/min, $\leq$ about 0.50 dg/min, $\leq$ about 0.25 dg/min, $\leq$ about 0.15 dg/min or $\leq$ about 0.10 dg/min. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 0.050 to about 12 dg/min, about 0.25 to about 5.0 dg/min, about 0.50 to about 8.0 dg/min, *etc.* In particular, a polymer blend described herein and/or an extrudate comprising the polymer blend as further described herein may have a melt index (I_{2.16}) of about 0.10 dg/min to about 10 dg/min.

Optional Additives

[0066] The polymer blends described above and/or the extrudate comprising the polymer blend as further described herein may be used in combination with other polymers, additives, processing aids, *etc.* For example, each layer may comprise a “neat” polymer with optional processing aids and/or additives or may comprise a blend of polymers with optional processing aids and/or additives.

[0067] In any embodiment, an additive may be present up to 1.0, or 2.0, or 3.0 wt% by weight of polymer films described herein. An additive may be added before, during, or after the formation of the polymer blend and/or extrudate.

First Antioxidant

[0068] The first antioxidant comprises one or more antioxidants. They include, but are not limited to, hindered phenols, for example, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (CAS 002082-79-3) commercially available as IRGANOX™ 1076, pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (CAS 6683-19-8) commercially available as IRGANOX™ 1010; and combinations thereof.

[0069] They may be combined with one or more polymers in range from 100 to 4000 parts by weight of the first antioxidant, based on one million parts of the polymer or polymer composition; alternatively, from 250 to 3000 parts by weight of the first antioxidant, based on one million parts of the polymer or polymer composition, alternatively, from 500 to 2500 parts by weight of the first antioxidant, based on one million parts of the polymer or polymer composition, alternatively, from 750 to 2500 parts by weight of the first antioxidant, based on

one million parts of the polymer or polymer composition, alternatively, from 750 to 2000 parts by weight of the first antioxidant, based on one million parts of the polymer or polymer composition, and alternatively, from 1000 to 2000 parts by weight of the first antioxidant, based on one million parts of the polymer or polymer composition.

5 Second Antioxidant

[0070] The second antioxidant comprises one or more antioxidants. They include, but are not limited to, liquid phosphites, such as C₂-C₇, preferably C₂-C₄, and alkyl aryl phosphites mixed structures. Non-limiting examples include mono-amyphenyl phosphites, di-amyphenyl phosphites, dimethylpropyl phosphites, 2-methylbutanyl phosphites, and
10 combinations thereof. In several embodiments of the invention, the second antioxidant may also be represented by the formula [4-(2-methylbutan-2-yl)phenyl]_x[2,4-bis(2-methylbutan-2-yl)phenyl]_{3-x} phosphate, wherein x=0, 1, 2, 3, or combinations thereof.

[0071] Such antioxidants and their use with polyolefin polymers have been described in U.S. Publication Nos. 2005/0113494, 2007/0021537, 2009/0326112, 2013/0190434,
15 2013/225738, 2014/0045981 and U.S. Patent Nos. 5,254,709, 6,444,836, 7,888,414, 7,947,769, 8,008,383, 8,048,946, 8,188,170, and 8,258,214. An example of a commercially available liquid phosphite is sold under the trade name WESTON™ 705 (Addivant, Danbury, Connecticut).

[0072] The second antioxidant may be combined with one or more polymers in the range
20 from 100 to 4000 parts by weight of the second antioxidant, based on one million parts of the polymer or polymer composition; alternatively, from 250 to 3000 parts by weight of the second antioxidant, based on one million parts of the polymer or polymer composition, alternatively, from 300 to 2000 parts by weight of the second antioxidant, based on one million parts of the polymer or polymer composition, alternatively, from 400 to 1450 parts by
25 weight of the second antioxidant, based on one million parts of the polymer or polymer composition, alternatively, from 425 to 1650 parts by weight of the second antioxidant, based on one million parts of the polymer or polymer composition, and alternatively, from 1 to 450 parts by weight of the second antioxidant, based on one million parts of the polymer or polymer composition.

30 [0073] The polymers and/or compositions comprising the first antioxidant and/or the second antioxidant described above may be used in combination with the following neutralizing agents, additional additives and other components.

Neutralizing Agents

[0074] One or more neutralizing agents (also called catalyst deactivators) include, but are not limited to, calcium stearate, zinc stearate, calcium oxide, synthetic hydrotalcite, such as DHT4A, and combinations thereof.

5 Additional Additives & Other Components

[0075] Additional additives and other components include, but are limited to, fillers (especially, silica, glass fibers, talc, etc.) colorants or dyes, pigments, color enhancers, whitening agents, UV stabilizers, cavitation agents, anti-slip agents, lubricants, plasticizers, processing aids, tackifiers, antistatic agents, acid scavengers (*e.g.*, calcium stearate),
10 antifogging agents, nucleating agents (both α -nucleators and β -nucleators), stabilizers such as lactone and vitamin E, mold release agents, other antioxidants (for example, hindered amines and phosphates), anti-blocking agents, anti-blooming agents, and other common additives as is known in the art. Nucleating agents include, for example, sodium benzoate, and talc. Slip agents include, for example, oleamide and erucamide. Additionally, flame retardant fillers
15 may be present in the composition, as described at Column 2 of US 5,430,091 and paragraphs [0044]-[0046] of WO 2012/030577.

[0076] In any embodiment, nucleating agents may be absent, and preferably, α -nucleating agents may be absent, meaning they are not added to the composition or any components of the composition at any stage of the process of formation. Examples of α -nucleating agents
20 include salts of monocarboxylic acids and polycarboxylic acids, sorbitols such as dibenzylidene sorbitol, salts of diesters of phosphoric acid, vinylcycloalkane polymers, and others as is known in the art.

Extrudates and Methods of Making the Extrudates

[0077] As discussed above, the polymer blends described herein may advantageously be
25 extruded at higher shearer rates to produce extrudates having a substantially smooth surface as well as a shiny or glossy surface. Thus, an extrudate comprising a polymer blend as described herein is provided. In particular, the extrudate may be a wire-coating (*e.g.*, low voltage (LV) insulation and jacketing) and/or a cable-coating. In various aspects, the extrudate can have an average thickness of $\leq$ about 5000 μm , $\leq$ about 4000 μm , $\leq$ about 2000
30 μm , $\leq$ about 1000 μm , $\leq$ about 500 μm , $\leq$ about 250 μm , $\leq$ about 1500 μm . Additionally, the extrudate can have an average thickness from about 100 μm to about 5000 μm , about 100 μm to about 2500 μm , about 150 μm to about 1000 μm . In an embodiment, the extrudate may have a smoothness as described in U.S. Patent No. 8,815,357.

[0078] In further embodiments, a method for preparing a polymer extrudate is also provided herein. The method may comprise blending a first polyethylene as described herein with a second polyethylene as described herein in amounts as previously described herein to form a blend. For example, the first polyethylene may comprise at least 80 mol% ethylene and have: a density of 0.910 g/cm³ to 0.96 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min, and the second polyethylene may comprise at least 80 mol% ethylene and have: a density of 0.915 g/cm³ to 0.970 g/cm³ and a melt index (I_{2.16}) of 0.01 dg/min to 10 dg/min.

[0079] In various aspects, the method may comprise extruding the blend under suitable conditions known to those of ordinary skill in the art to form the polymer extrudate. For example, the blend may be extruded via single or twin screw extrusion. Advantageously, the blend may be extruded at higher shear rates without experiencing a high degree of shear flow deformation, *e.g.*, at a shear rate $\geq$ about 500 s⁻¹, $\geq$ about 800 s⁻¹, $\geq$ about 1000 s⁻¹, $\geq$ about 2000 s⁻¹, $\geq$ about 3000 s⁻¹, $\geq$ about 4000 s⁻¹, $\geq$ about 5000 s⁻¹, $\geq$ about 6000 s⁻¹, $\geq$ about 7000 s⁻¹, $\geq$ about 8000 s⁻¹, $\geq$ about 9000 s⁻¹, or $\geq$ about 10000 s⁻¹. Additionally, the blend may be extruded at a shear rate of $\leq$ about 10000 s⁻¹, $\leq$ about 9000 s⁻¹, $\leq$ about 8000 s⁻¹, $\leq$ about 7000 s⁻¹, $\leq$ about 6000 s⁻¹, $\leq$ about 5000 s⁻¹, $\leq$ about 4000 s⁻¹, $\leq$ about 3000 s⁻¹, $\leq$ about 2000 s⁻¹, $\leq$ about 1000 s⁻¹, or $\leq$ about 800 s⁻¹. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 500 s⁻¹ to about 10000 s⁻¹, about 800 s⁻¹ to about 10000 s⁻¹, about 1000 s⁻¹ to about 9000 s⁻¹, about 1000 s⁻¹ to about 8000 s⁻¹, *etc.*

[0080] Additionally or alternatively, the blend may be extruded at a melt temperature $\leq$ about 300°C, $\leq$ about 275°C, $\leq$ about 250°C, $\leq$ about 225°C, $\leq$ about 200°C, $\leq$ about 190°C, $\leq$ about 180°C, or $\leq$ about 160°C. Additionally, the blend may be extruded at a melt temperature $\geq$ about 150°C, $\geq$ about 160°C, $\geq$ about 180°C, $\geq$ about 190°C, $\geq$ about 200°C, $\geq$ about 225°C, $\geq$ about 250°C, or $\geq$ about 275°C. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations of any of the above-enumerated values, *e.g.*, from about 150°C to about 300°C, about 160°C to about 250°C, about 180°C to about 225°C, or about 180°C to about 200°C.

[0081] In a particular embodiment, the blend may be extruded at a shear rate $\geq$ about 800 s⁻¹ and a melt temperature $\leq$ about 200°C and/or a shear rate $\geq$ about 3000 s⁻¹ and a melt temperature $\leq$ about 190°C.

[0082] In another embodiment, a polymer extrudate produced according the above-described method is provided herein. In particular, the polymer extrudate may be a wire-coating (*e.g.*, low voltage (LV) insulation and jacketing) and/or a cable-coating.

Other End Use Applications

[0083] In addition to using the inventive polymer blend composition and extrudate in wire/cable applications (as described in U.S. Patent No. 6,270,856), the inventors appreciate that the following additional end-uses described herein. Various other articles are provided
5 herein, which comprise a polymer blend as described above. In various aspects, the polymer blend may be extruded to form films that optionally can comprise additional polymer layers to form multi-layered films or multi-layered sheets, which may be used to further form various articles, such as but not limited to thermoformed articles, blow molded articles and/or foamed articles. As used herein, “multi-layered” refers to structures including two or more
10 polymers each forming a flat surface having an average thickness, the same or different, that have been combined together and caused to adhere to one another such as by application of radiation, heat, or use of adhesives to form a single multi-layer structure; preferably formed by a process of coextrusion utilizing two or more extruders to melt and deliver a steady volumetric throughput of different viscous polymers to a single extrusion head (die) which
15 will extrude the materials in the desired form.

[0084] In any embodiment, a thermoformed article comprising a polymer blend described herein is provided. Thermoforming is a fabrication process which involves heating a sheet(s) of material such as a polyolefin and forming it over a male or female mold. The two basic types of thermoforming processes—vacuum forming and pressure forming, and derivative
20 processes such as twin sheet thermoforming—make plastic thermoforming a broad and diverse plastic forming process. Thermoformed plastics are suited for automotive, consumer products, packaging, retail and display, sports and leisure, electronics, and industrial applications. The most advantageous aspects of thermoforming are its low tooling and engineering costs and fast turnaround time which makes thermoforming or vacuuumforming
25 ideal for prototype development and low-volume production. Non-limiting examples of thermoformed articles comprising multi-layered sheets described herein include pallets, tubs, dunnage, food containers (especially frozen food containers), and other durable goods.

[0085] In any embodiment, a blow molded article is provided herein, which comprises a polymer blend described herein. Blow molding is a molding process in which air pressure is
30 used to inflate soft plastic into a mold cavity. It is a useful process for making one-piece hollow plastic parts with thin walls, such as bottles and similar containers. Since many of these items are used for consumer beverages for mass markets, production is typically organized for very high quantities. The technology is borrowed from the glass industry with which plastics compete in the disposable or recyclable bottle market. Blow molding is

accomplished in at least two steps: (1) fabrication of a starting tube of molten material, called a parison; and (2) inflation of the tube to the desired final shape. Forming the parison is accomplished by either of two processes: extrusion or injection molding.

[0086] Extrusion blow molding typically consists of a cycle of 4 to 6 steps. In most cases, the process is organized as a very high production operation for making plastic bottles. The sequence is automated and usually integrated with downstream operations such as bottle filling and labeling. It is preferred that the blown container be rigid, and rigidity depends on wall thickness and the nature of the materials being used. The steps in extrusion blow molding can include: (1) extrusion of parison; (2) parison is pinched at the top and sealed at the bottom around a metal blow pin as the two halves of the mold come together; (3) the tube is inflated so that it takes the shape of the mold cavity; and (4) mold is opened to remove the solidified part.

[0087] In injection blow molding, the starting parison is injection molded rather than extruded. A simplified sequence is outlined below. Compared to its extrusion-based competitor, the injection blow-molding process has a lower production rate. The steps of injection blow molding can include: (1) parison is injection molded around a blowing rod; (2) injection mold is opened and parison is transferred to a blow mold; (3) soft polymer is inflated to conform to a blow mold; and (4) blow mold is opened and blown product is removed. Non-limiting examples of blow molded articles comprising multi-layered sheets described herein include drums, bottles, hollow panels, sheds and utility structures.

[0088] In any embodiment, a profile is provided herein, which comprises a polymer blend described herein. Profile extrusion is extrusion of a shaped product that can be a variety of configurations, and can include solid forms as well as hollow forms. Products ranging from tubing to window frames to vehicle door seals are manufactured this way and considered profile extrusion. To process hollow profiled shapes, a pin or mandrel is utilized inside the die to form the hollow section or sections. Multiple hollow sections require multiple pins. To create these hollow sections a source of positive air pressure is required to allow the center of the product to maintain shape and not collapse in a vacuum. When two or more materials are required to make a product, the co-extrusion process is preferably used. For example, a white drinking straw that has two colors of stripes, requires a total of three extruders. Each extruder feeds a different material or variation of the same material into a central co-extrusion die. Non-limiting examples of articles made from (comprising, or consisting of) a profile comprising at least one layer of a high melt strength polypropylene

described herein includes pipes, structural frames, siding, tubing, decking, window and door frames (fenestration).

[0089] In any embodiment, a foamed article is provided herein, which comprises a polymer blend described herein. For example, the polymers described herein (*e.g.*, first
5 polyethylene, second polyethylene) may further comprise a foaming agent as is known in the art to effect the formation of air containing pockets or cells within the composition, thus creating an “expanded” or “foamed” films, sheet and/or profile, and article made therefrom. In any embodiment the sheets and/or articles described herein are the reaction product of a foaming agent within the polymer making up the films, sheets, profiles and/or articles made
10 therefrom. This reaction product may be formed into any number of suitable foamed articles such as cups, plates, other food containing items, and food storage boxes, toys, handle grips, automotive components, and other articles of manufacture as described herein.

[0090] The various descriptive elements and numerical ranges disclosed herein for the inventive multi-layered structures and methods of forming such can be combined with other
15 descriptive elements and numerical ranges to describe the invention(s); further, for a given element, any upper numerical limit can be combined with any lower numerical limit described herein, including the examples in jurisdictions that allow such combinations. The features of the inventions are demonstrated in the following non-limiting examples.

EXAMPLES

20 [0091] Extrudates (Sample 1 and Comparative Samples 1–7) were produced with a HAAKE 252 Single Screw Extruder using a screw rotation speed of 200 rpm, which corresponds to an apparent die wall shear rate of $\sim 6,400 \text{ s}^{-1}$. The screw diameter was $\frac{3}{4}$ inch, the ratio of length to screw diameter (L/D) was 25:1. The compression ratio was 3:1. A rod die with a diameter of 1.5 mm was used, and the cylindrical strand was passed through a
25 water bath then recovered manually. The mass throughput was determined in lbs/hr by collection and weighing pellets exiting the pelletizer over a period of time, typically 1 minute. Extrudates that were composed of blends of polyethylene were generated by blending pellets of pure components, which were then fed into the extruder hopper.

[0092] To assess the processability and melt fracture performance, a HAAKE 252 single
30 screw extruder was used. The screw diameter was $\frac{3}{4}$ inch, the ratio of length over screw diameter (L/D) was 25:1, and the compression ratio was 3:1. A rod die was used with a diameter of 1.5 mm, and the cylindrical strand exiting the die was collected on a steel board. The mass throughput was determined in lbs/hr by collecting and weighing pellets exiting the pelletizer over a period of time, typically 1 minute. Melt temperature as described in

paragraphs [0078]-[0079] and Table 2 was measured in the bulk of the melt with an infrared sensor at a location between the end of the screw and the die.

[0093] The extrudate compositions are shown below in Table 1. Enable™ 2010CB (metallocene polyethylene resin), Paxon™ BA46-055 (high density polyethylene), LL 3003.32 (linear low density polyethylene resin), Exceed™ 3518CB (metallocene polyethylene resin), and LD 103.09 (low density polyethylene) were obtained from ExxonMobil Chemical Company, Houston, Texas. DFDA 7530 (linear low density polyethylene resin) was obtained from Dow Chemical Company.

[0094] Extruder conditions for the inventive Sample 1 and Comparative Samples 1-7 of Table 1 are provided in Table 2, below.

Table 1

Sample	Composition
Sample 1	80% Enable™ 2010CB + 20% Paxon™ BA46-055
Comparative Sample 1	100% Enable™ 2010CB
Comparative Sample 2	100% LL 3003.32
Comparative Sample 3	80% Enable™ 2010CB + 20% Exceed™ 3518CB
Comparative Sample 4	80% Enable™ 2010CB + 20% LL 3003.32
Comparative Sample 5	80% Enable™ 2010CB + 20% LD 103.09
Comparative Sample 6	100% Ex 2a (as described in US Patent No. 9,284,415, Table 2)
Comparative Sample 7	100% DFDA 7530

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Table 2

Sample	Sample 1	Comparative Sample 1	Comparative Sample 2	Comparative Sample 3	Comparative Sample 4	Comparative Sample 5	Comparative Sample 6	Comparative Sample 7
Barrel Zone 1 (C)	181	182	180	181	181	181	181	180
Barrel Zone 2 (C)	192	193	190	192	190	190	192	190
Barrel Zone 2 (C)	216	214	206	216	211	211	216	206
Die Zone (C)	220	220	220	220	220	220	220	220
Melt Temperature (C)	184	185	182	187	182	182	184	180
Screw Speed (RPM)	200	200	200	200	200	200	200	200
Head Pressure (PSI)	1989	1826	1388	1789	1724	1826	1989	1653
Throughput (grams/min)	87.8	95.7	97.4	94.6	97.1	N/A	87.8	97.9

[0095] Optical microscopy pictures of the extrudates (Sample 1, Comparative Samples 1–7) were taken and are shown in FIGS. 1a–7b. Stereo-optical microscopy images were acquired using an Olympus SZX-12 stereo microscope equipped with a 0.055 numerical aperture Plan Fluorite 0.5X objective and Leica DFC295 camera. A ring light was used to provide reflected lighting. The camera settings and aperture stop settings were held constant for all translucent white samples. Various lighting conditions were used for the colored samples to provide adequate contrast.

[0096] It was surprisingly discovered that a blend of 80% Enable™ 2010CB with 20% Paxon™ BA46-55 (Sample 1) produced a very smooth and shiny/glossy extrudate compared to 100% Enable™ 2010CB (Comparative Sample 1), 100% LL 3003.32 (Comparative Sample 2) and blends of 80% Enable™ 2010CB and 20% Exceed™ 3518CB (Comparative Sample 3), 80% Enable™ 2010CB and 20% LL 3003.32 (Comparative Sample 4), 80% Enable™ 2010CB and 20% LD 103.09 (Comparative Sample 5), all of which produced a rough extrudate. Additionally, Sample 1 was surprisingly smoother than an extrudate of DFDA 7530 (Comparative Sample 7), a linear low density polyethylene resin commonly used for wire coating applications in North and South America as well as Ex 2a (Comparative Sample 6), an oxygen tailored version of Enable™ 2005 as disclosed in WO 2013/137953.

[0097] For all jurisdictions in which the doctrine of “incorporation by reference” applies, all of the test methods, patent publications, patents and reference articles are hereby incorporated by reference either in their entirety or for the relevant portion for which they are referenced.

CLAIMS

1. A polymer blend comprising:
a first polyethylene comprising at least 80 mol% ethylene and having: a density of 0.910 g/cm³ to 0.960 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min; and
5 a second polyethylene comprising at least 80 mol% ethylene and having: a density of 0.915 g/cm³ to 0.970 g/cm³ and a melt index (I_{2.16}) of 0.01 dg/min to 10 dg/min,
wherein the polymer blend has a density of 0.910 g/cm³ to 0.965 g/cm³ and a melt index (I_{2.16}) of 0.10 dg/min to 10 dg/min.
- 10 2. The polymer blend of claim 1, wherein the first polyethylene comprises at least 90 mol% ethylene and the second polyethylene comprises at least 90 mol% ethylene.
3. The polymer blend of any one of the preceding claims, wherein the first polyethylene has a molecular weight distribution (M_w/M_n) within the range from 2 to 6 and/or the second
15 polyethylene has a molecular weight distribution (M_w/M_n) within the range from 7 to 30.
4. The polymer blend of any one of the preceding claims, wherein the second polyethylene has a high load melt index (I_{21.6}) of 1.0 dg/min to 60 dg/min.
- 20 5. The polymer blend of any one of the preceding claims, wherein the first polyethylene is present in an amount of about 50 wt% to about 99 wt%, based on the total weight of the polymer blend, and the second polyethylene is present in an amount of about 1.0 wt% to about 50 wt%, based on the total weight of the polymer blend.
- 25 6. The polymer blend of any one of the preceding claims, wherein the first polyethylene is present in an amount of about 60 wt% to about 80 wt%, based on the total weight of the polymer blend, and the second polyethylene is present in an amount of about 20 wt% to about 40 wt%, based on the total weight of the polymer blend.
- 30 7. An extrudate comprising the polymer blend of any preceding claim.
8. The extrudate of claim 7, having an average thickness of less than 5000 μm.

9. The extrudate of claim 7 or claim 8, wherein the extrudate is formed at a shear rate of $\geq 800 \text{ s}^{-1}$ and a melt temperature of $\leq 200^\circ\text{C}$.
10. The extrudate of any one of claims 7-9, wherein the extrudate is a cable-coating
5 and/or a wire-coating.
11. A method for preparing a polymer extrudate comprising:
blending a first polyethylene comprising at least 80 mol% ethylene and having: a
density of 0.910 g/cm^3 to 0.96 g/cm^3 and a melt index ($I_{2.16}$) of 0.10 dg/10 min to 10 dg/min
10 with a second polyethylene comprising at least 80 mol% ethylene and having: a density of
 0.915 g/cm^3 to 0.970 g/cm^3 and a melt index ($I_{2.16}$) of 0.01 dg/min to 10 dg/min ; and
extruding the blend at a shear rate of $\geq 800 \text{ s}^{-1}$ and a melt temperature of $\leq 200^\circ\text{C}$,
wherein the polymer extrudate has a density of 0.910 g/cm^3 to 0.965 g/cm^3 and a melt index
($I_{2.16}$) of 0.10 dg/min to 10 dg/min .
15
12. The method of claim 11, wherein the shear rate is $\geq 3000 \text{ s}^{-1}$ and/or the melt
temperature of $\leq 190^\circ\text{C}$.
13. The method of any one of claims 11-12, wherein the first polyethylene comprises at
20 least 90 mol% ethylene and the second polyethylene comprises at least 90 mol% ethylene.
14. The method of any one of claims 11-13, wherein the first polyethylene has a
molecular weight distribution (M_w/M_n) within the range from 2 to 6 and/or the second
polyethylene has a molecular weight distribution (M_w/M_n) within the range from 7 to 30.
25
15. The method of any one of claims 11-14, wherein the second polyethylene has a high
load melt index ($I_{21.6}$) of 1.0 dg/min to 60 dg/min .
16. The method of any one of claims 11-15, wherein the first polyethylene is blended in
30 an amount of about 50 wt% to about 99 wt%, based on the total weight of the polymer blend,
and the second polyethylene is blended in an amount of about 1.0 wt% to about 50 wt%,
based on the total weight of the polymer blend.

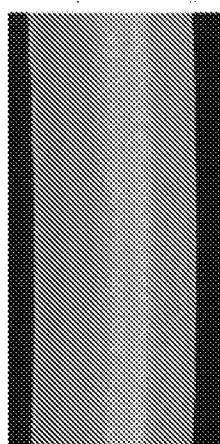
17. The method of any one of claims 11-16, wherein the first polyethylene is blended in an amount of about 60 wt% to about 80 wt%, based on the total weight of the polymer blend, and the second polyethylene is blended in an amount of about 20 wt% to about 40 wt%, based on the total weight of the polymer blend.

5

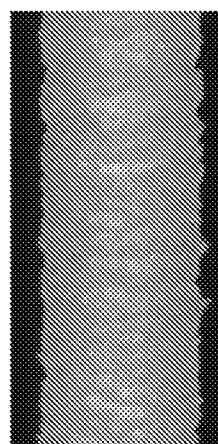
18. A polymer blend extrudate produced according to the method of any one of claims 11-17.

19. The polymer blend extrudate of claim 18, wherein the extrudate is a cable-coating
10 and/or a wire-coating.

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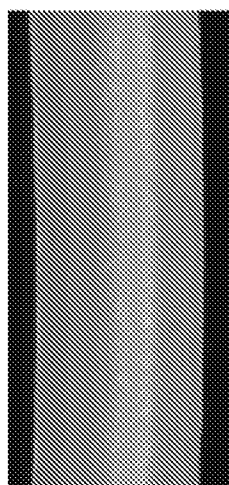
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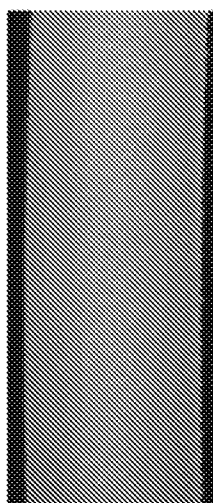
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FIG. 1

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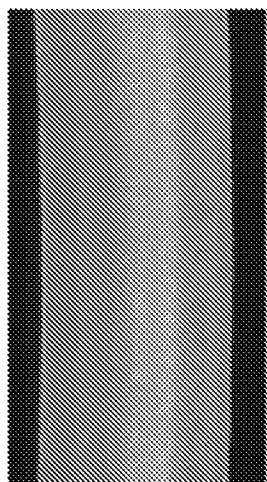
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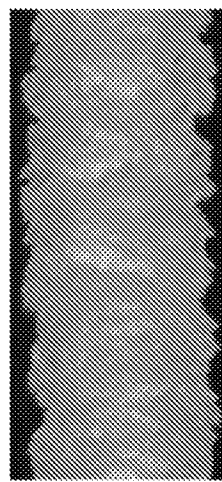
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FIG. 2

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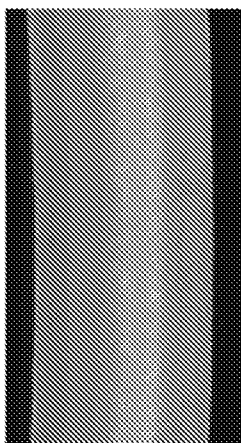
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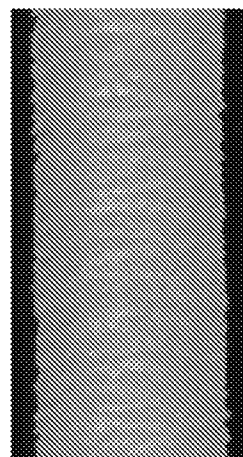
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FIG. 3

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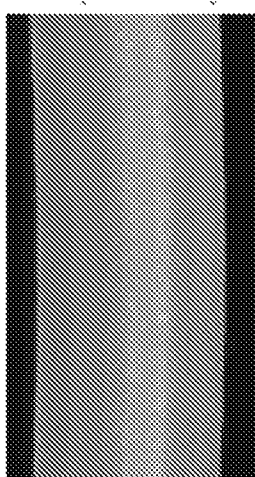
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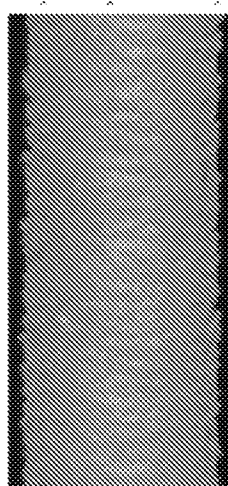
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FIG. 4

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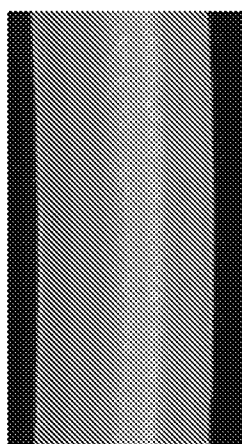
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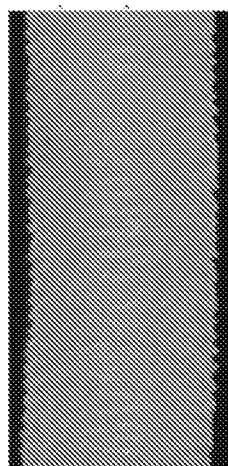
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FIG. 5

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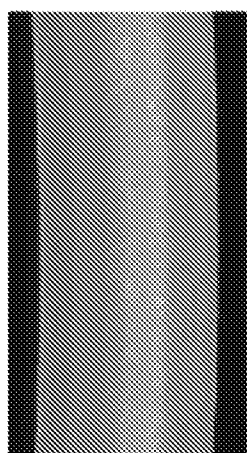
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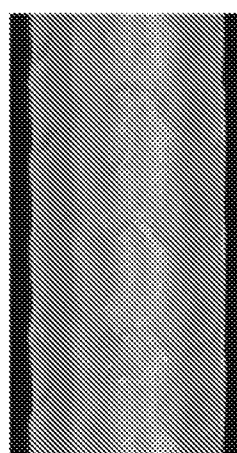
b.

FIG. 6

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a.



b.

FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/027325

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/08
ADD.

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)
C08L

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/113496 A1 (HARRIS MICHAEL G [US] ET AL) 19 June 2003 (2003-06-19) page 6; examples 1-3; table 1 page 6, paragraph 53-62; examples 1-3 paragraphs [0004], [0019], [0024], [0027], [0041] claims 1,24,27	1-19
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

17 July 2018

Date of mailing of the international search report

25/07/2018

Name and mailing address of the ISA/

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/027325

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2014/003925 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 3 January 2014 (2014-01-03) page 11; example Inv.Cpstns. 1 and 2; table 2 page 10; examples BLLDPE,MLLDPE; table 1 page 9; example Inv.Cpstns. 1 and 2 -----	1-19
E	WO 2018/118741 A2 (DOW GLOBAL TECHNOLOGIES LLC [US]) 28 June 2018 (2018-06-28) page 24 - page 26; examples; tables 2-4 page 21; table 1A paragraphs [0001] - [0006], [0012], [0025] -----	1-19
X,P	EP 3 182 419 A1 (BOREALIS AG [AT]) 21 June 2017 (2017-06-21) page 9; example 1; table 1 paragraphs [0001] - [0004], [0069], [0070], [0076] -----	1-19

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Information on patent family members

International application No

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