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HIGH MELT STRENGTH POLYETHYLENE WITH AN ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE COMPONENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of U.S. Provisional Application Serial No. 63/510,774 filed June 28, 2023, the contents of which is incorporated in its entirety herein.

TECHNICAL FIELD

[002] Embodiments described in this disclosure generally relate to films having a high melt strength and, more specifically, relate to films produced from high melt strength polyethylene resins with an ultra-high molecular weight component.

BACKGROUND

[003] High melt strength is an advantageous property in polyethylene resins, as it improves the processability of the material. Low density polyethylene (LDPE), made via a radical process, typically exhibits high melt strength, but the LDPE resins generally have poor mechanical properties. In contrast, linear low-density polyethylene (LLDPE), made via solution or gas phase processes, typically has poor melt strength but excellent mechanical properties. To combat the issues surrounding LLDPE and LDPE, some amount of LDPE is typically blended into LLDPE in order to improve the processability of LLDPE resins. Unfortunately, the addition of LDPE leads to significant decreases in the mechanical properties of the resulting blends when compared with the superior performance of the LLDPE resin.

SUMMARY

[004] Conventional films produced from LLDPE and LDPE blended resins have a higher melt strength, however, with the addition of the LDPE, the mechanical properties of the films are reduced when compared to films produced from conventional LLDPE resins.

[005] Melt strength and processability are correlated properties of polyethylene resins. In general, a higher melt strength provides for a polyethylene resin with improved processability.

[006] Additionally, conventional polyethylene resins produced by conventional processes typically see a tradeoff between the resin's mechanical properties and melt strength. For example, conventional radical processes, which are known to be hazardous, produce low density polyethylene (LDPE) that typically exhibit high melt strength but have poor mechanical properties. In contrast, linear low-density polyethylene (LLDPE) made via solution or gas phase processes typically have poor melt strength but excellent mechanical properties.

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[007] Therefore, to increase processability, some amount of LDPE may typically be blended with LLDPE in order to improve the processability and melt strength of LLDPE resins. Unfortunately, the addition of LDPE leads to a decrease in the mechanical properties of the resulting blends when compared with pure LLDPE resin.

[008] Accordingly, there are needs for films having a high dart strength with high processability when compared to LLDPE and UHMWPE blends.

[009] Embodiments of this disclosure include films comprising a polyethylene multimodal resin. The polyethylene multimodal resin includes the polymerized reaction product of ethylene and at least one alpha-olefin copolymer. The polyethylene multimodal resin includes a melt strength (MS) $\geq X_1/I_2 + y$, wherein X_1 is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and wherein the film comprises a normalized dart strength (DS) greater than or equal to 9,876 minus 10,512 times the density of the polyethylene multimodal resin ($DS \geq 9,876 - 10,512(\rho)$, wherein DS is measured according to ASTM 1709).

[0010] In some embodiments, the film includes a polyethylene multimodal resin. The polyethylene multimodal resin includes the polymerized reaction product of ethylene and at least one alpha-olefin copolymer. In one or more embodiments, the polyethylene multimodal resin may have a melt strength (MS) $\geq x/I_2 + y$, in which x is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle). In various embodiments, the film includes a normalized machine direction (MD) tear of greater than 85 gf/mil, wherein MD tear is measured according to ASTM D1922-15.

[0011] These and embodiments are described in more detail in the following Detailed Description in conjunction with the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

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[0013] FIG. 1 schematically depicts a reactor system useful for producing polyethylene, according to one or more embodiments presently described;

[0014] FIG. 2 is a graphical depiction of the melt strength as a function of melt flow (I_2) of the examples of this description and comparative examples, including blends of LLDPE and HDPE and single resin polymers.

[0015] FIG. 3 is a graphical depiction of the normalized dart strength as a function of density of the examples of this description and comparative examples, including blends of LLDPE and HDPE and single resin polymers.

DETAILED DESCRIPTION

[0016] Specific embodiments of the present application will now be described. These embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the claimed subject matter to those skilled in the art.

[0017] The term “polymer” refers to a polymeric compound prepared by polymerizing monomers, whether of a same or a different type. The generic term polymer thus embraces the term “homopolymer,” which usually refers to a polymer prepared from only one type of monomer as well as “copolymer,” which refers to a polymer prepared from two or more different monomers. The term “interpolymer,” as used herein, refers to a polymer prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes a copolymer or polymer prepared from more than two different types of monomers, such as terpolymers.

[0018] “Polyethylene” or “ethylene-based polymer” shall mean polymers comprising greater than 50% by mole of units derived from ethylene monomer. This includes ethylene-based homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of ethylene-based polymers known in the art include, but are not limited to, Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m- LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE).

[0019] The term “composition,” as used herein, refers to a mixture of materials that comprises the composition, as well as reaction products and decomposition products formed from the materials of the composition.

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[0020] “Polypropylene” or “propylene-based polymer” as used herein, refers to a polymer that comprises, in polymerized form, greater than 50% by mole of units that have been derived from propylene monomer. This includes propylene homopolymer, random copolymer polypropylene, impact copolymer polypropylene, propylene/ α -olefin copolymer, and propylene/ α -olefin copolymer.

[0021] The term “LDPE” may also be referred to as “high pressure ethylene polymer” or “highly branched polyethylene” and is defined to mean that the polymer is partly or entirely homopolymerized or copolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators, such as peroxides (*see*, for example, U.S. Patent No. 4,599,392, which is hereby incorporated by reference in its entirety). LDPE resins typically have a density in the range of 0.916 g/cm³ to 0.940 g/cm³.

[0022] The term “LLDPE,” includes resin made using Ziegler-Natta catalyst systems as well as resin made using single-site catalysts, including, but not limited to, bis-metallocene catalysts (sometimes referred to as “m-LLDPE”), phosphinimine, and constrained geometry catalysts, and resins made using post-metallocene, molecular catalysts, including, but not limited to, bis(biphenylphenoxy) catalysts (also referred to as polyvalent aryloxyether catalysts). LLDPE includes linear, substantially linear, or heterogeneous ethylene-based copolymers or homopolymers. LLDPEs contain less long chain branching than LDPEs and include the substantially linear ethylene polymers, which are further defined in U.S. Patent No. 5,272,236, U.S. Patent No. 5,278,272, U.S. Patent No. 5,582,923 and U.S. Patent No. 5,733,155 each of which are incorporated herein by reference in their entirety; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992 which is incorporated herein by reference in its entirety; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698 which is incorporated herein by reference in its entirety; and blends thereof (such as those disclosed in U.S. Patent No. 3,914,342 and U.S. Patent No. 5,854,045 which are incorporated herein by reference in their entirety). The LLDPE resins can be made via gas-phase, solution-phase, or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

[0023] The term “Selected MDPE” refers to polyethylenes having densities from 0.924 g/cm³ to 0.936 g/cm³, as described in more detail subsequently herein.

[0024] The term “HDPE” refers to polyethylenes having densities greater than 0.935 g/cm³ and up to 0.980 g/cm³, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts or single-site catalysts including, but not limited to, substituted mono- or bis-cyclopentadienyl catalysts (typically referred to as metallocene), constrained geometry catalysts, phosphinimine catalysts & polyvalent aryloxyether catalysts (typically referred to as bisphenyl phenoxy).

[0025] The term “ULDPE” refers to polyethylenes having densities of 0.855 g/cm³ to 0.912 g/cm³, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts, or single-site catalysts including, but not limited to, substituted mono- or bis-cyclopentadienyl catalysts (typically referred to as metallocene), constrained geometry catalysts, phosphinimine catalysts & polyvalent aryloxyether catalysts (typically referred to as bisphenyl phenoxy). ULDPEs include, but are not limited to, polyethylene (ethylene-based) plastomers and polyethylene (ethylene-based) elastomers. Polyethylene (ethylene-based) elastomers plastomers generally have densities of 0.855 g/cm³ to 0.912 g/cm³.

[0026] “Blend,” “polymer blend,” and like terms mean a composition of two or more polymers. Such a blend may or may not be miscible. Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and any other method known in the art. Blends are not laminates, but one or more layers of a laminate may contain a blend. Such blends can be prepared as dry blends, formed in situ (*e.g.*, in a reactor), melt blends, or using other techniques known to those of skill in the art.

[0027] The term “multimodal” refers to polymers produced from a plurality of polymer fractions, each polymer fraction being produced by a distinct catalyst in a distinct reaction environment. Multimodal may include bimodal polymers having two polymer fractions, trimodal ethylene-based polymers having three polymer fractions, or polymers having more than three polymer fractions.

[0028] “Multilayer structure” or “multilayer film” means any structure having more than one layer. For example, the multilayer structure (for example, a film) may have two, three, four, five, six, seven, or more layers. A multilayer structure may be described as having the layers designated with letters. For example, a three-layer structure designated as A/B/C may have a core layer, (B), and two external layers, (A) and (C).

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[0029] The terms “comprising,” “including,” “having,” and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term “comprising” may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed.

[0030] Embodiments of the present disclosure include films comprising a polyethylene multimodal resin. The polyethylene multimodal resin includes the polymerized reaction product of ethylene and at least one alpha-olefin copolymer. The polyethylene multimodal resin includes a melt strength (MS) $\geq X_1/I_2 + y$, wherein X_1 is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and wherein the film comprises a dart strength (DS) greater than or equal to 9,876 minus 10,512 times the density of the polyethylene multimodal resin ($DS \geq 9,876 - 10,512(\rho)$), wherein DS is measured according to ASTM 1709 Method A with dart type A.

[0031] In some embodiments, the film includes a polyethylene multimodal resin. The polyethylene multimodal resin includes the polymerized reaction product of ethylene and at least one alpha-olefin copolymer. In one or more embodiments, the polyethylene multimodal resin may have a melt strength (MS) $\geq x/I_2 + y$, in which x is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle). In various embodiments, the film includes a normalized machine direction (MD) tear of greater than 85 gf/mil, wherein MD tear is measured according to ASTM D1922-15.

[0032] In one or more embodiments, the multimodal resin does not include an additional polymer resin that is added in a post reactor blending method. The blending methods may include, but are not limited to, dry blending, melt processing, or combinations thereof.

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[0033] According to embodiments, the polyethylene multimodal resin composition may have a melt strength (MS) that satisfies the following equation 1:

$$MS \geq \frac{x}{I_2} + y \quad (\text{EQ. 1})$$

[0034] In equation 1, x is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C. According to one or more embodiments, the multimodal ethylene-based copolymer composition may have a melt strength of at least 5 centiNewtons (cN). In further embodiments, the multimodal ethylene-based copolymer composition may have a melt strength of from 5 cN to 50 cN, from 5 cN to 45 cN, from 5 cN to 40 cN, from 5 cN to 35 cN, from 5 cN to 30 cN, from 5 cN to 25 cN, from 5 cN to 20 cN, from 5 cN to 15 cN, from 5 cN to 10 cN, from 10 cN to 50 cN, from 10 cN to 45 cN, from 10 cN to 40 cN, from 10 cN to 35 cN, from 10 cN to 30 cN, from 10 cN to 25 cN, from 10 cN to 20 cN, from 10 cN to 15 cN, from 15 cN to 50 cN, from 15 cN to 45 cN, from 15 cN to 40 cN, from 15 cN to 35 cN, from 15 cN to 30 cN, from 15 cN to 25 cN, from 15 cN to 20 cN, from 20 cN to 50 cN, from 20 cN to 45 cN, from 20 cN to 40 cN, from 20 cN to 35 cN, from 20 cN to 30 cN, from 20 cN to 25 cN, from 25 cN to 50 cN, from 25 cN to 45 cN, from 25 cN to 40 cN, from 25 cN to 35 cN, from 25 cN to 30 cN, from 30 cN to 50 cN, from 30 cN to 45 cN, from 30 cN to 40 cN, from 30 cN to 35 cN, from 35 cN to 50 cN, from 35 cN to 45 cN, from 35 cN to 40 cN, from 40 cN to 50 cN, from 40 cN to 45 cN, or from 45 cN to 50 cN.

[0035] In embodiments, the polyethylene multimodal resin may have a ratio of viscosity measured at 0.1 radians/second and 190 °C to viscosity measured at 100 radians/second and 190 °C ($V_{0.1}/V_{100}$), as determined by dynamic mechanical analysis, of less than or equal to 6. In some embodiments, the polyethylene multimodal resin may have a viscosity ratio of $V_{0.1}/V_{100}$, as determined by dynamic mechanical analysis, of less than 5, from 6 to 1, from 6 to 2, from 6 to 3, from 6 to 4, from 6 to 5, from 5 to 1, from 5 to 2, from 5 to 3, from 5 to 4, from 4 to 1, from 4 to 2, from 4 to 3, from 3 to 1, or from 3 to 2 or from 2 to 1.

[0036] In one or more embodiments, the polyethylene multimodal resin may have a melt index (I_2) of from 0.50 g/10 minutes (g/10 min) to 10.0 g/10 min when measured according to ASTM D-1238 at 190 °C and 2.16 kg. In one or more embodiments, the multimodal ethylene-based copolymer composition may have a melt index (I_2) of from 0.5 g/10 min to 10.0 g/10 min, from 0.5 g/10 min to 9.0 g/10 min, from 0.5 g/10 min to 8.0 g/10 min, from 0.5 g/10 min to 7.0 g/10 min, from 0.5 g/10 min to 6.0 g/10 min, from 0.5 g/10 min to 5.0 g/10 min, from

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0.5 g/10 min to 4.0 g/10 min, from 0.5 g/10 min to 3.0 g/10 min, from 0.5 g/10 min to 2.0 g/10 min, from 0.5 g/10 min to 1.0 g/10 min, from 1.0 g/10 min to 10.0 g/10 min, from 1.0 g/10 min to 9.0 g/10 min, from 1.0 g/10 min to 8.0 g/10 min, from 1.0 g/10 min to 7.0 g/10 min, from 1.0 g/10 min to 6.0 g/10 min, from 1.0 g/10 min to 5.0 g/10 min, from 1.0 g/10 min to 4.0 g/10 min, from 1.0 g/10 min to 3.0 g/10 min, from 1.0 g/10 min to 2.0 g/10 min, from 2.0 g/10 min to 10.0 g/10 min, from 2.0 g/10 min to 9.0 g/10 min, from 2.0 g/10 min to 8.0 g/10 min, from 2.0 g/10 min to 7.0 g/10 min, from 2.0 g/10 min to 6.0 g/10 min, from 2.0 g/10 min to 5.0 g/10 min, from 2.0 g/10 min to 4.0 g/10 min, from 2.0 g/10 min to 3.0 g/10 min, from 3.0 g/10 min to 10.0 g/10 min, from 3.0 g/10 min to 9.0 g/10 min, from 3.0 g/10 min to 8.0 g/10 min, from 3.0 g/10 min to 7.0 g/10 min, from 3.0 g/10 min to 6.0 g/10 min, from 3.0 g/10 min to 5.0 g/10 min, from 3.0 g/10 min to 4.0 g/10 min, from 4.0 g/10 min to 10.0 g/10 min, from 4.0 g/10 min to 9.0 g/10 min, from 4.0 g/10 min to 8.0 g/10 min, from 4.0 g/10 min to 7.0 g/10 min, from 4.0 g/10 min to 6.0 g/10 min, from 4.0 g/10 min to 5.0 g/10 min, from 5.0 g/10 min to 10.0 g/10 min, from 5.0 g/10 min to 9.0 g/10 min, from 5.0 g/10 min to 8.0 g/10 min, from 5.0 g/10 min to 7.0 g/10 min, from 5.0 g/10 min to 6.0 g/10 min, from 6.0 g/10 min to 10.0 g/10 min, from 6.0 g/10 min to 9.0 g/10 min, from 6.0 g/10 min to 8.0 g/10 min, from 6.0 g/10 min to 7.0 g/10 min, from 7.0 g/10 min to 10.0 g/10 min, from 7.0 g/10 min to 9.0 g/10 min, from 7.0 g/10 min to 8.0 g/10 min, from 8.0 g/10 min to 10.0 g/10 min, from 8.0 g/10 min to 9.0 g/10 min, from 9.0 g/10 min to 10.0 g/10 min, or any combination of these ranges, when measured according to ASTM D-1238 at 190 °C and 2.16 kg.

[0037] In embodiments, the film includes a normalized dart strength (DS) greater than or equal to 9,876 minus 10,512 times the density of the polyethylene multimodal resin ($DS \geq 9,876 - 10,512(\rho)$), wherein normalized DS is measured in gram (g) according to ASTM 1709 Method A divided by the film thickness in mils.

[0038] The film may include a normalized dart strength (DS) 9,876 minus 10,512 times the density of the polyethylene multimodal resin ($DS \geq 9,876 - 10,512(\rho)$), wherein normalized DS is measured in gram (g) according to ASTM 1709 Method A divided by the film thickness in mils. This relationship between normalized dart strength and density of the polyethylene multimodal resin is depicted in FIG. 3. The normalized DS of the film may be from 15 to 1000 g/mil, or from 20 to 1000 g/mil.

[0039] In some embodiments, the film includes a dart strength greater than 800 g as measured according to ASTM 1709 Method A with dart type A. In one or more embodiments,

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the dart strength is greater than 900 g, greater than 1000 g, or greater than 1200 g. In various embodiments, the film includes a dart strength of from 800 g to 5000 g. In some embodiments, the film includes a dart strength from 800 g to 2000 g, from 800 g to 1800, from 800 g to 1600 g, from 800 g to 1500 g, from 800 g to 1200 g, from 800 g to 1000 g, from 800 g to 900 g, from 850 g to 2000 g, from 850 g to 1800, from 850 g to 1600 g, from 850 g to 1500 g, from 850 g to 1200 g, from 850 g to 1000 g, from 850 g to 900 g, from 900 g to 2000 g, from 900 g to 1800, from 900 g to 1600 g, from 900 g to 1500 g, from 900 g to 1200 g, or from 900 g to 1000 g.

[0040] In one or more embodiments, the film includes a normalized machine direction (MD) tear of greater than 85 gf/mil, wherein MD tear is measured according to ASTM D1922-15. In some embodiments, the film includes a normalized MD tear of greater than 90 gf/mil, greater than 100 gf/mil, greater than 120 gf/mil, greater than 150 gf/mil, or greater than 200 gf/mil. In various embodiments, the film includes a normalized MD tear of from 85 gf/mil to 1000 gf/mil, from 85 gf/mil to 500 gf/mil, from 85 gf/mil to 400 gf/mil, from 85 gf/mil to 300 gf/mil, from 85 gf/mil to 200 gf/mil, from 85 gf/mil to 100 gf/mil, from 90 gf/mil to 500 gf/mil, from 90 gf/mil to 400 gf/mil, from 90 gf/mil to 300 gf/mil, from 90 gf/mil to 200 gf/mil, or from 90 gf/mil to 100 gf/mil.

[0041] In various embodiments, the polyethylene multimodal resin has a melt flow ratio (I_{10}/I_2) of greater than 5. In some embodiments, the polyethylene multimodal resin has a melt flow ratio of greater than 7. In some embodiments, the polyethylene multimodal resin has a melt flow ratio of greater from 5 to 10. In some embodiments, the polyethylene multimodal resin has a melt flow ratio of from 5 to 9, from 5 to 8, from 5 to 7, from 5 to 6, from 6 to 10, from 6 to 9, from 6 to 8, from 6 to 7, from 7 to 10, from 7 to 9, from 7 to 8, from 8 to 10, from 8 to 9, or from 9 to 10.

[0042] In some embodiments, the polyethylene multimodal resin comprises a density of from 0.900 to 0.975 g/cc or 0.910 to 0.930 g/cc. In various embodiments, the polyethylene multimodal resin comprises a density of from 0.0915 to 0.950 or 0.0900 to 0.950; and in one or more embodiments, the polyethylene multimodal resin comprises a density of from 0.0915 to 0.930.

[0043] In one or more embodiments, the polyethylene multimodal resin has a density greater than or equal to 0.918 g/cc, a melt strength of at least 7 cN, and a melt flow ratio (I_{10}/I_2) greater than 5, and wherein the film has a dart strength of greater than 300 g.

[0044] In some embodiments, the polyethylene multimodal resin has a density from 0.910 to 0.930 g/cc, a melt strength of at least 7 cN, and a melt flow ratio (I_{10}/I_2) from 5 to 10, and wherein the film has dart strength of greater than 800 g.

[0045] In various embodiments, the polyethylene multimodal resin has a melt strength of at least 7 cN, and the film has a machine direction tear of greater than 85 gf/mil as measured according to ASTM D1922-15.

[0046] In one or more embodiments, the polyethylene multimodal resin has a melt strength of at least 8 cN, and a rheology ratio $V_{0.1}/V_{100}$ of less than or equal to 6, and wherein the film has a dart strength of greater than 800 g, wherein $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second.

[0047] In embodiments, the polyethylene multimodal resin has an overall density of from 0.918 to 0.925 g/cc, a melt strength greater than or equal to 6 cN, and an (M_z/M_w) of greater than or equal to 2, wherein M_z is the Z- average molecular weight and M_w is the weight average molecular weight are measured according to Gel Permeation Chromatography.

[0048] It should be understood that the polyethylene multimodal resin may further include one or more additives as known to those of skill in the art such as, for example, plasticizers, stabilizers including viscosity stabilizers, hydrolytic stabilizers, primary and secondary antioxidants, ultraviolet light absorbers, anti-static agents, dyes, pigments or other coloring agents, inorganic fillers, fire-retardants, lubricants, reinforcing agents such as glass fiber and flakes, synthetic (for example, aramid) fiber or pulp, foaming or blowing agents, processing aids, slip additives, antiblock agents such as silica or talc, release agents, tackifying resins, or combinations of two or more thereof. Inorganic fillers, such as calcium carbonate, and the like can also be incorporated into the film. In some embodiments, the polyethylene multimodal resin may each include up to 5 weight percent of such additional additives based on the total weight of the respective layer. All individual values and subranges from 0 wt.% to 5 wt.% are included and disclosed herein; for example, the total amount of additives in the first layer, the second layer, or the third layer can be from 0.5 wt.% to 5 wt.%, from 0.5 wt.% to 4 wt.%, from 0.5 wt.% to 3 wt.%, from 0.5 wt.% to 2 wt.%, from 0.5 wt.% to 1 wt.%, from 1 wt.% to 5 wt.%, from 1 wt.% to 4 wt.%, from 1 wt.% to 3 wt.%, from 1 wt.% to 2 wt.%, from 2 wt.% to 5 wt.%, from 2 wt.% to 4 wt.%, from 2 wt.% to 3 wt.%, from 3 wt.% to 5 wt.%, from 3 wt.% to 4 wt.%, or from 4 wt.% to 5 wt.% based on the total weight of the respective layer. The incorporation

of the additives can be carried out by any known process such as, for example, by dry blending, by extruding a mixture of the various constituents, by the conventional master batch technique, or the like.

[0049] The polyethylene multimodal resin may be blended with a low density polyethylene (LDPE) resin to produce a polyethylene blend. The low density polyethylene may have a melt index from 0.1 g/10 min to 10.0 g/10 min when measured according to ASTM D1238 at a load of 2.16 kg and temperature of 190 °C. The low density polyethylene may have a melt index from 0.1 g/10 min to 5.0 g/10 min, or from 0.5 g/10 min to 5.0 g/10 min, or from 0.5 g/10 min to 2.0 g/10 min. The low density polyethylene (LDPE) may have a density of from having a density from 0.910 to 0.930 g/cc or 0.915 g/cm³ to 0.930 g/cm³ when measured according to ASTM D792. The LDPE may have a density from 0.910 g/cm³ to 0.925 g/cm³ or from 0.915 g/cm³ to 0.930 g/cm³.

[0050] In one or more embodiments, the films of the present disclosure may be a monolayer film.

[0051] The films of the present disclosure can have a variety of thicknesses. The thickness of the film may depend on a number of factors including, for example, the number of layers in the film, the composition of the layers in the multilayer film, the desired properties of the film, the desired end-use application of the film, the manufacturing process of the film, and others. In embodiments, the film may have a thickness of less than 205 micrometers (μm or microns). In embodiments, the multilayer film may have a thickness of from 15 μm to 205 μm, from 20 μm to 180 μm, from 15 μm to 180 μm, from 15 μm to 160 μm, from 15 μm to 140 μm, from 15 μm to 120 μm, from 15 μm to 100 μm, from 15 μm to 80 μm, from 15 μm to 60 μm, from 15 μm to 40 μm, from 20 μm to 160 μm, from 20 μm to 140 μm, from 20 μm to 120 μm, from 20 μm to 100 μm, from 20 μm to 80 μm, from 20 μm to 60 μm, or from 20 μm to 40 μm.

Multilayer Films

[0052] Embodiments of this disclosure include multilayer films. In some embodiments, the multilayer films may include two, three, four or five layers and as many as seven, nine, eleven, thirteen or more layers. The number of layers in the multilayer film may depend on a number of factors including, for example, the composition of each layer in the multilayer film, the desired properties of the multilayer film, the end-use application of the multilayer film, the manufacturing process of the multilayer film, and others. As described in more detail herein, embodiments of the multilayer film may include a barrier layer; one or more outer layers, as

described subsequently in this disclosure; and one or more subskin layers. The one or more subskin layers may include a Selected medium density polyethylene (MDPE) described in detail herein below. The Selected MDPE in the one or more subskin layers may be the same or different in composition.

[0053] The multilayer film may be a three-layer film designated as A/B/C or A/B/A, for example; or the multilayer film may be a five-layer film designated as A/B/C/D/E, where the first layer may be designated as (A), the second layer may be designated as (B), the third layer may be designated as (C), the fourth layer may be designated as (D), and the fifth layer may be designated as (E). In embodiments, layer (C) may be referred to as a “middle layer” or “core layer.” In embodiments, layer (C) may be a barrier layer, as described subsequently in this disclosure. In embodiments, one or both of layer (A) and layer (E) may be outer layers, as described subsequently in this disclosure. In embodiments, one or both of layer (B) and layer (D) may be subskin layers, as described subsequently in this disclosure.

[0054] In one or more embodiments, the film further includes a low density polyethylene (LDPE) resin layer. In one or more embodiments, the low density polyethylene may have a melt index from 0.1 g/10 min to 10.0 g/10 min when measured according to ASTM D1238 at a load of 2.16 kg and temperature of 190 °C. In embodiments, the low density polyethylene may have a melt index from 0.1 g/10 min to 5.0 g/10 min, or from 0.5 g/10 min to 5.0 g/10 min, or from 0.5 g/10 min to 2.0 g/10 min.

[0055] In some embodiments, the low density polyethylene (LDPE) may have a density of from having a density from 0.910 to 0.930 g/cc or 0.915 g/cm³ to 0.930 g/cm³ when measured according to ASTM D792. In another embodiment, the LDPE may a density from 0.910 g/cm³ to 0.925 g/cm³ or from 0.915 g/cm³ to 0.930 g/cm³.

[0056] It should be understood that any of the foregoing layers may further comprise one or more additives as known to those of skill in the art such as, for example, plasticizers, stabilizers including viscosity stabilizers, hydrolytic stabilizers, primary and secondary antioxidants, ultraviolet light absorbers, anti-static agents, dyes, pigments or other coloring agents, inorganic fillers, fire-retardants, lubricants, reinforcing agents such as glass fiber and flakes, synthetic (for example, aramid) fiber or pulp, foaming or blowing agents, processing aids, slip additives, antiblock agents such as silica or talc, release agents, tackifying resins, or combinations of two or more thereof. Inorganic fillers, such as calcium carbonate, and the like can also be incorporated into one or more of the first layer, the second layer, the third layer,

and combinations thereof. In some embodiments, each of the layers may each include up to 5 weight percent of such additional additives based on the total weight of the respective layer. All individual values and subranges from 0 wt.% to 5 wt.% are included and disclosed herein; for example, the total amount of additives in the first layer, the second layer, or the third layer can be from 0.5 wt.% to 5 wt.%, from 0.5 wt.% to 4 wt.%, from 0.5 wt.% to 3 wt.%, from 0.5 wt.% to 2 wt.%, from 0.5 wt.% to 1 wt.%, from 1 wt.% to 5 wt.%, from 1 wt.% to 4 wt.%, from 1 wt.% to 3 wt.%, from 1 wt.% to 2 wt.%, from 2 wt.% to 5 wt.%, from 2 wt.% to 4 wt.%, from 2 wt.% to 3 wt.%, from 3 wt.% to 5 wt.%, from 3 wt.% to 4 wt.%, or from 4 wt.% to 5 wt.% based on the total weight of the respective layer. The incorporation of the additives can be carried out by any known process such as, for example, by dry blending, by extruding a mixture of the various constituents, by the conventional master batch technique, or the like.

[0057] The multilayer films of the present disclosure can have a variety of thicknesses. The thickness of the multilayer film may depend on a number of factors including, for example, the number of layers in the multilayer film, the composition of the layers in the multilayer film, the desired properties of the multilayer film, the desired end-use application of the film, the manufacturing process of the multilayer film, and others. In embodiments, the multilayer film may have a thickness of less than 205 micrometers (μm or microns). In embodiments, the multilayer film may have a thickness of from 15 μm to 205 μm , from 20 μm to 180 μm , from 15 μm to 180 μm , from 15 μm to 160 μm , from 15 μm to 140 μm , from 15 μm to 120 μm , from 15 μm to 100 μm , from 15 μm to 80 μm , from 15 μm to 60 μm , from 15 μm to 40 μm , from 20 μm to 160 μm , from 20 μm to 140 μm , from 20 μm to 120 μm , from 20 μm to 100 μm , from 20 μm to 80 μm , from 20 μm to 60 μm , or from 20 μm to 40 μm .

Processes

[0058] In embodiments, the polyethylene multimodal resin may be produced via a solution polymerization process. In embodiments, the process of making a polyethylene multimodal resin may include contacting at least two olefinic monomers in the presence of a catalyst system comprising at least one low molecular weight catalyst and at least one high molecular weight catalyst in the solution polymerization reactor system.

[0059] In embodiments, the solution polymerization reactor system may include one or more reactors. In embodiments, the solution polymerization reactor system may be a dual reactor system. In embodiments that comprise a dual reactor system, the solution polymerization reactor system may include a first reactor and a second reactor. Such solution

polymerization processes include using one or more conventional reactors such as loop reactors, isothermal reactors, adiabatic reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0060] In embodiments, ethylene and at least one olefinic monomer may be polymerized in the presence of a catalyst to produce the polyethylene multimodal resin described herein. The olefinic monomer may be an α -olefin co-monomers. Typically, the α -olefin monomers have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene. In embodiments, the α -olefin co-monomers and the process solvent may be purified with molecular sieves before introduction into the solution polymerization reactor system. The solvent, monomer, comonomers, and hydrogen may be combined and feed to the solution polymerization reactor system. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR™ E from ExxonMobil Chemical. In embodiments, the combined feed may be temperature controlled to a temperature of from 5 °C to 50 °C, from 5 °C to 25 °C, from 5 °C to 10 °C, from 10 °C to 50 °C, from 10 °C to 25 °C, or from 25 °C to 50°C.

Methods of Producing the Presently-Described Films

[0061] Various methodologies are contemplated for producing the films of this disclosure. In one or more embodiments, the process of manufacturing the multilayer film may include cast film extrusion or blown film extrusion.

[0062] In some embodiments, the process of manufacturing the film may include forming a blown film bubble. In some embodiments, the blown film bubble may be a multilayer blown film bubble. Further in accordance with this embodiment, the multilayer blown film bubble may include at least five, seven, nine, or more layers, and the layers may adhere to each other.

[0063] Embodiments of the blown film process include an extruded film from an extruder die may be formed (blown) and pulled up a tower onto a nip. The film may then be wound onto a core. Before the film is wound onto the core, the ends of the film may be cut and folded using

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folding equipment. This makes the layers of the film difficult to separate, which may be important for shipping applications, generally, or heavy duty shipping sack applications.

[0064] In further embodiments, the blown film bubble may be formed via a blown film extrusion line having a length to diameter (“L/D”) ratio of from 30 to 1. In some embodiments, the extrusion line may have a blow up ratio of from 1 to 5, from 1 to 3, from 2 to 5, or from 2 to 3. In some embodiments, the extrusion line may utilize a die with internal bubble cooling. In some embodiments, the die gap may be from 1 millimeter (mm) to 5 mm, from 1 mm to 3 mm, from 2 mm to 5 mm, or from 2 mm to 3 mm.

[0065] In some embodiments, the extrusion line may utilize a film thickness gauge scanner. In some embodiments, during the extrusion process, the multilayer film thickness may be maintained at from 15 μm or to 115 μm . In embodiments, the multilayer film thickness may be maintained at from 15 μm to 100 μm , from 15 μm to 75 μm , from 15 μm to 50 μm , from 15 μm to 25 μm , from 25 μm to 115 μm , from 25 μm to 100 μm , from 25 μm to 75 μm , from 25 μm to 50 μm , from 50 μm to 115 μm , from 50 μm to 100 μm , from 50 μm to 75 μm , from 75 μm to 115 μm , from 75 μm to 100 μm , or from 100 μm to 115 μm .

[0066] In some embodiments, the forming of the multilayer blown film bubble step may occur at a temperature of from 350 to 500 °F, or from 375 to 475 °F. The output speed may be from 5 lb/hr/in to 25 lb/hr/in, from 5 lb/hr/in to 20 lb/hr/in, from 5 lb/hr/in to 15 lb/hr/in, from 5 lb/hr/in to 10 lb/hr/in, from 10 lb/hr/in to 25 lb/hr/in, from 10 lb/hr/in to 20 lb/hr/in, from 10 lb/hr/in to 15 lb/hr/in, from 15 lb/hr/in to 25 lb/hr/in, from 15 lb/hr/in to 20 lb/hr/in, or from 20 lb/hr/in to 25 lb/hr/in.

Blown Film Line Description: Line 1

[0067] Two mil blown films were made using a monolayer Dr. Collin blown film line. The line comprises a 30:1 L/D single screw extruder, equipped with grooved feed zones, and a 30 mm screw diameter. The annular die was 60 mm in diameter and used a dual lip air ring cooling system. The die lip gap was 2 mm and the blow up ratio (BUR) was 2.0. The lay flat width was around 48 cm. The frost line height was 5-6 inches. The total output rate was 5-8 kg/hour. The melt temperature was 200-220 °C, and the die temperature was set at 225°C.

Blown Film Line Description: Line 2

[0068] Gravimetric feeders are dosed resin formulations into a Labtech LTE20-32 twin screw extruder at rate of 15 lbs/hr. From the extruder, the resin formulation is conveyed into the 2” die diameter die with gap of 1.0 mm. The Labtech feed throat is set to 193°C and the

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remaining barrel, conveying portion, and die temperature were set and maintained to 215°C. Pressurized ambient air is used to inflate the film bubble to a 2.5 blow-up ratio. A dual lip air ring driven by a variable speed blower is used for all experiments. The frost line height (FLH) was maintained between 8.8 and 10.8 inches. Film thickness was targeted at 2 mils and was controlled within $\pm 15\%$ by adjusting the nip roller speed. The films are wound up into a roll.

Articles

[0069] Embodiments of the present disclosure also relate to articles, such as packages, formed from the multilayer films of the present disclosure. Such packages can be formed from any of the multilayer films of the present disclosure described herein. Multilayer films of the present disclosure are particularly useful in articles where good tear strength and dart strength are desired.

[0070] Examples of such articles can include flexible packages, pouches, stand-up pouches, and pre-made packages or pouches.

[0071] Various methods of producing embodiments of articles from the multilayer films disclosed herein would be familiar to one of ordinary skill in the art.

Catalyst Systems

[0072] Specific embodiments of catalyst systems that can, in one or more embodiments, be used to produce the polyethylene compositions described herein will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0073] The term “procatalyst” refers to a compound that has catalytic activity when combined with an activator. The term “activator” refers to a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active catalyst. As used herein, the terms “co-catalyst” and “activator” are interchangeable terms.

[0074] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₄₀)alkyl is an alkyl group having from 1 to 40 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by

one or more substituents such as R^S . An R^S substituted version of a chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S . For example, a “(C₁–C₄₀)alkyl substituted with exactly one group R^S , where R^S is phenyl (–C₆H₅)” may contain from 7 to 46 carbon atoms. Thus, in general when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S , the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S .

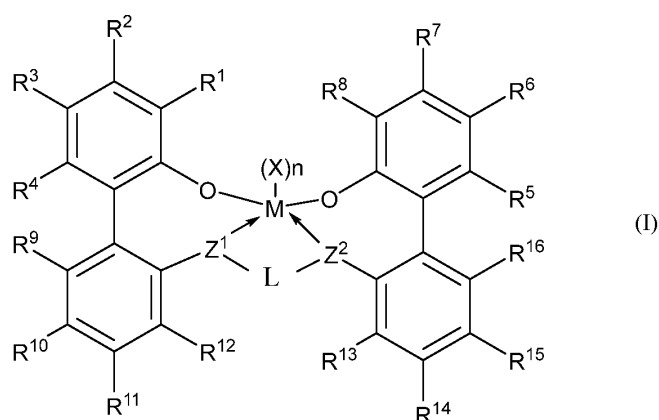
[0075] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or function group is replaced by a substituent (e.g. R^S). The term “persubstitution” means that every hydrogen atom (H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The term “polysubstitution” means that at least two, but fewer than all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding unsubstituted compound or functional group are replaced by a substituent.

[0076] The term “–H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “–H” are interchangeable, and unless clearly specified mean the same thing.

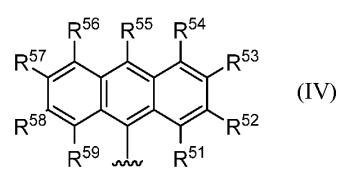
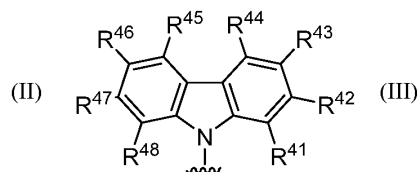
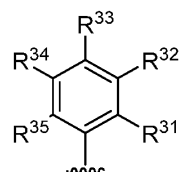
[0077] The terms “halogen atom,” “halogen,” “halide,” “saturated,” “unsaturated,” ““(C₁–C₅₀)hydrocarbyl,” ““(C₁–C₅₀)alkyl,” ““(C₁–C₁₈)alkyl,” ““(C₆–C₅₀)aryl,” ““(C₃–C₅₀)cycloalkyl,” ““(C₁–C₅₀)alkylene,” “heteroatom,” and ““(C₁–C₅₀)heteroalkyl” are as defined in publication number WO2020185494A1.

[0078] According to some embodiments, a catalyst system for producing a polyethylene composition includes a metal–ligand complex according to formula (I):

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[0079] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal being in a formal oxidation state of +2, +3, or +4; n is 0, 1, or 2; when n is 1, X is a monodentate ligand or a bidentate ligand; when n is 2, each X is a monodentate ligand and is the same or different; the metal–ligand complex is overall charge-neutral; each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$; L is $(\text{C}_1\text{--C}_{40})$ hydrocarbylene or $(\text{C}_1\text{--C}_{40})$ heterohydrocarbylene, wherein the $(\text{C}_1\text{--C}_{40})$ hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone linking the two Z groups in Formula (I) (to which L is bonded) or the $(\text{C}_1\text{--C}_{40})$ heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone linking the two Z groups in Formula (I), wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the $(\text{C}_1\text{--C}_{40})$ heterohydrocarbylene independently is a carbon atom or heteroatom, wherein each heteroatom independently is O, S, S(O), S(O)₂, Si(R^C)₂, Ge(R^C)₂, P(R^C), or N(R^C), wherein independently each R^C is $(\text{C}_1\text{--C}_{30})$ hydrocarbyl or $(\text{C}_1\text{--C}_{30})$ heterohydrocarbyl; R¹ and R⁸ are independently selected from the group consisting of $-\text{H}$, $(\text{C}_1\text{--C}_{40})$ hydrocarbyl, $(\text{C}_1\text{--C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{N}})_2\text{NC}(\text{O})-$, halogen, and radicals having formula (II), formula (III), or formula (IV):



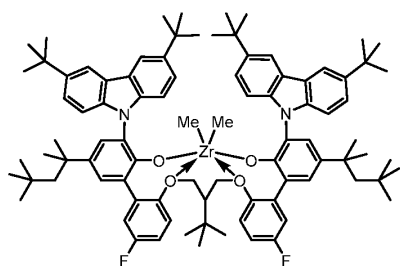
[0080] In formulas (II), (III), and (IV), each of R^{31–35}, R^{41–48}, or R^{51–59} is independently chosen from $(\text{C}_1\text{--C}_{40})$ hydrocarbyl, $(\text{C}_1\text{--C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$,

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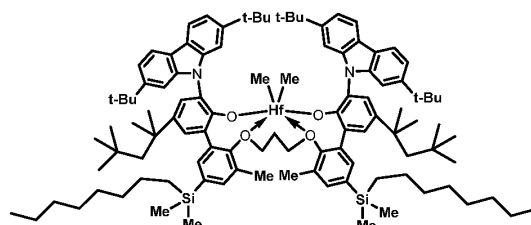
$-\text{N}(\text{R}^{\text{N}})_2$, $-\text{N}=\text{CHR}^{\text{C}}$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{N}})_2\text{NC}(\text{O})-$, halogen, or $-\text{H}$, provided at least one of R^1 or R^8 is a radical having formula (II), formula (III), or formula (IV).

[0081] In formula (I), each of R^{2-4} , R^{5-7} , and R^{9-16} is independently selected from $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{N}=\text{CHR}^{\text{C}}$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, and $-\text{H}$.

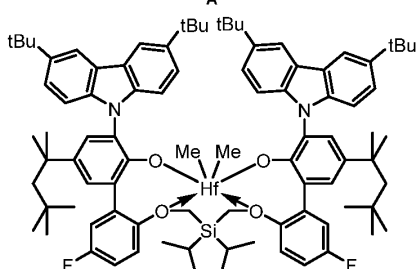
[0082] In some embodiments, the multimodal base resin is formed using a first catalyst according to formula (I) in a first reactor and a different catalyst according to formula (I) in a second reactor.



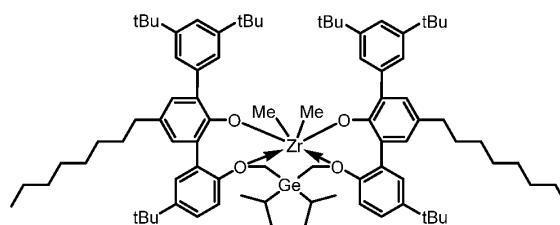
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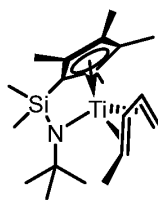
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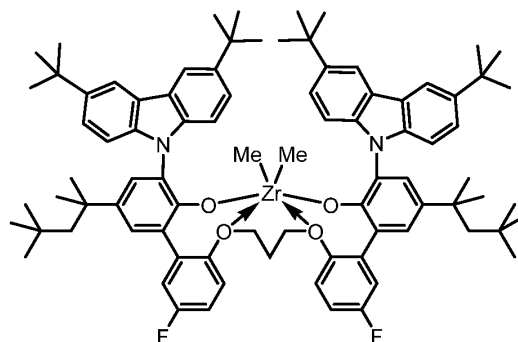
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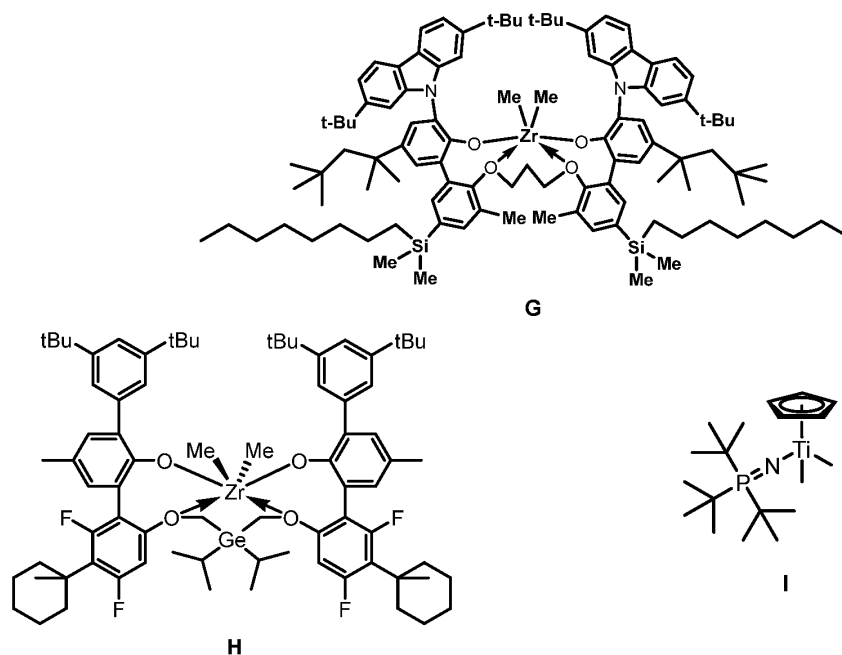


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Co-Catalyst Component

[0083] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0084] Lewis acid activators (co-catalysts) include Group 13 metal compounds containing from 1 to 3 (C₁–C₂₀)hydrocarbyl substituents as described herein. In one embodiment, Group 13 metal compounds are tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum or tri((C₁–C₂₀)hydrocarbyl)-boron compounds. In embodiments, Group 13 metal compounds are

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tri(hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof. In further embodiments, Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tris((C₁–C₂₀)hydrocarbyl borate (e.g. trityl tetrafluoroborate) or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra((C₁–C₂₀)hydrocarbyl)borane (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺, a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[0085] Combinations of neutral Lewis acid activators (co-catalysts) include mixtures comprising a combination of a tri((C₁–C₄)alkyl)aluminum and a halogenated tri((C₆–C₁₈)aryl)boron compound, especially a tris(pentafluorophenyl)borane. Embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Ratios of numbers of moles of (metal–ligand complex) : (tris(pentafluoro-phenyl)borane): (alumoxane) [e.g., (Group 4 metal–ligand complex) : (tris(pentafluoro-phenyl)borane):(alumoxane)] are from 1:1:1 to 1:10:30, in embodiments, from 1:1:1.5 to 1:5:10

[0086] The catalyst system comprising the metal–ligand complex of formula (I) may be activated to form an active catalyst composition by combination with one or more co-catalysts, for example, a cation forming co-catalyst, a strong Lewis acid, or combinations thereof. Suitable activating co-catalysts include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to: modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1[−]) amine, and combinations thereof.

[0087] In some embodiments, one or more of the foregoing activating co-catalysts are used in combination with each other. An especially preferred combination is a mixture of a tri((C₁–C₄)hydrocarbyl)aluminum, tri((C₁–C₄)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of

one or more metal-ligand complexes of formula (I) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some embodiments, at least 1:1000; and 10:1 or less, and in some embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the metal-ligand complex of formula (I). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal-ligand complexes of formula (I) from 0.5: 1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal-ligand complexes of formula (I).

Continuous Solution Polymerization Reactions: Setup 1

[0088] Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent SBP 100/140, commercially available from Shell Chemicals) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure at 525 psig. The solvent and comonomer (1-octene) feeds are pressurized via mechanical positive displacement pump to above reaction pressure at 525 psig. MMAO-3A, commercially available from AkzoNobel, was used as an impurity scavenger. The individual catalyst components (procatalyst and cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (SBP 100/140), in some cases 4 equivalents of triethylaluminum was added to the procatalyst solution, and they are pressured to above reaction pressure at 525 psig. The cocatalyst is $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, commercially available from Boulder Scientific, and was used at a 1.2 molar ratio relative to the procatalyst. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

[0089] Continuous solution polymerizations are carried out in a 5 liters (L) continuously stirred-tank reactor (CSTR). In some cases, reactions were performed in two such reactors connected either in series or in parallel. The reactor has independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to the reactor is temperature controlled to anywhere

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between 5 °C to 50 °C and typically 25 °C or 50 °C. The fresh comonomer feed to the polymerization reactor is fed in with the solvent feed. The fresh solvent feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The co-catalyst is fed based on a calculated specified molar ratio (1.2 molar equivalents) to the procatalyst component. Immediately following each fresh injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The effluent from the polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits the first reactor loop and passes through a control valve (responsible for maintaining the pressure of the first reactor at a specified target). As the stream exits the reactor it is contacted with water to stop the reaction. In addition, various additives such as antioxidants, could be added at this point. The stream then went through another set of static mixing elements to evenly disperse the catalyst kill and additives.

[0090] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passed through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then enters a two-stage separation and devolatilization system where the polymer is removed from the solvent, hydrogen, and unreacted monomer and comonomer. The separated and devolatilized polymer melt is pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a box for storage.

Continuous Solution Polymerization Reactions: Setup 2

[0091] All raw materials (monomer and comonomer) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, Isopar-E) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied pressurized as a high purity grade and is not further purified. The reactor monomer feed stream is pressurized via a mechanical compressor to above reaction pressure. The solvent and comonomer feed is pressurized via a pump to above reaction pressure. The individual catalyst components are manually batch diluted with purified solvent and pressured to above reaction pressure. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

[0092] A two reactor system is used in a series configuration. The first reactor is a continuous solution polymerization reactor consisting of a liquid full, adiabatic, continuously

stirred tank reactor (CSTR). Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the second reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the second polymerization reactor is injected into the reactor at one location. The catalyst components are injected into the second polymerization reactor separate from the fresh feed. The primary catalyst component feed is computer controlled to maintain the reactor monomer conversion at the specified value. The cocatalyst component(s) is/are fed based on molar ratios to the primary catalyst component. Mixing of the second reactor is provided by an agitator. The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the first reactor loop and is added to the second reactor separate from the fresh feed and separate from the catalyst feed components.

[0093] The second reactor is a continuous solution polymerization reactor consisting of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the first reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the first polymerization reactor is injected into the reactor at two locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor separate from the fresh feeds. The primary catalyst component feed is computer controlled to maintain the reactor monomer conversion at the specified value, and to produce a polymer with a desired MI, density, and melt strength. The cocatalyst component(s) is/are fed based on molar ratios to the primary catalyst component. Immediately following each first reactor feed injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of the first reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around the first reactor loop is provided by a pump.

[0094] The second reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (water). Antioxidant addition can also occur at this same addition point. Following catalyst deactivation and additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The isolated polymer melt is pelletized and collected. The non-polymer stream passes through various pieces of equipment which separate most of the ethylene which is removed from the system. Most of the solvent and unreacted comonomer is recycled back to the reactor after passing through a purification system. A small amount of solvent and comonomer is purged from the process.

[0095] The reactor stream feed data flows that correspond to the values in Table 3. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram.

Procedure for Compounding Resins

[0096] The compounding process was carried out using a Thermo micro-16 twin-screw compounder. Samples were compounded specifically for fabricating film on a blown film line and for testing using analytical techniques such as GPC (Gel Permeation Chromatography) and rheology measurements. The compounding process was conducted under carefully controlled conditions to ensure optimal results. The Micro-16 Extruder was set with specific temperature zones. Zone 1 was set at approximately 140 °C, Zone 2 at approximately 150 °C, Zone 3 at approximately 160 °C, Zone 4 at approximately 170 °C, Zone 5 at approximately 180 °C, Zone 6 at approximately 180 °C, Zone 7 at approximately 205 °C, Zone 8 at approximately 205 °C, Zone 9 at approximately 212 °C, and Zone 10 at approximately 200 °C. The die temperature was maintained at around approximately 180 °C. The extruder operated at 400 rpm. Extruders were operated at a rate of 2.7 lbs/hr.

Blown Film Line Description: Line 1

[0097] 2 mil blown films were made using a monolayer Dr. Collin blown film line. The line comprises a 30:1 L/D single screw extruder, equipped with grooved feed zones, and a 30 mm screw diameter. The annular die was 60 mm in diameter and used a dual lip air ring cooling system. The die lip gap was 2 mm and the blow up ratio (BUR) was 2.0. The lay flat width was around 48 cm. The frost line height was 5-6 inches. The total output rate was 5-8 kg/hour. The melt temperature was 200-220 °C, and the die temperature was set at 225 °C.

Blown Film Line Description: Line 2

[0098] Gravimetric feeders dosed resin formulations into a Labtech LTE20-32 twin screw extruder at rate of 15 lbs/hr. From the extruder the resin formulation is conveyed into the 2" die diameter die with gap of 1.0 mm. The LTE feed throat was set to 193 °C and the remaining barrel, conveying portion, and die temperature were set and maintained to 215 °C. Pressurized ambient air inflated the film bubble to a 2.5 blow-up ratio. A dual lip air ring driven by a variable speed blower is used for all experiments. The frost line height (FLH) was maintained between 8.8 and 10.8 inches. Film thickness was targeted at 2 mils and was controlled within $\pm 15\%$ by adjusting the nip roller speed. The films are wound up into a roll.

TEST METHODS

[0099] The test methods include the following:

Melt index

[00100] Melt indices I_2 (or $I2$) and I_{10} (or $I10$) of polymer samples were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively. Their values are reported in g/10 min. Fractions of polymer samples were measured by collecting product polymer from the reactor which produces that specific fraction or portion of the polymer composition. For example, the first polyethylene fraction can be collected from the reactor producing the lower density, higher molecular weight component of the polymer composition. The polymer solution is dried under vacuum before the melt index measurement.

Density

[00101] Samples for density measurement were prepared according to ASTM D4703. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

Haze

[00102] Prior to testing the samples are conditioned for a minimum of 40hrs at 23 (+/- 2) °C and 50 (+/-10) % R.H. per ASTM D618 (Procedure A).

[00103] Haze is measured on a 6 inch x 6 inch specimen cut from the film sheet. The thickness is measured at the center of the specimen. The specimen is presented at the haze port of a BYK Hazegard-I testing machine, and the haze measured in accordance with ASTM D1003. Typically ten replicates are measured and the average and standard deviation reported.

Elmendorf MD Tear

[00104] MD Tear was measured according to ASTM D-1922. The force in grams required to propagate tearing across a film specimen is measured using a Elmendorf Tear tester. Acting

by gravity, the pendulum swings through an arc, tearing the specimen from a precut slit. The tear is propagated in the cross direction. Samples are conditioned for a minimum of 40 hours at temperature prior to testing.

[00105] Normalized Elmendorf MD Tear is calculated by dividing the Elmendorf MD Tear value by the thickness of the film.

ASTM D1709 Dart Drop

[00106] The film Dart Drop test determines the energy that causes plastic film to fail under specified conditions of impact by a free falling dart. The test result is the energy, expressed in terms of the weight of the missile falling from a specified height, which would result in failure of 50% of the specimens tested.

[00107] After the film is produced, it is conditioned for at least 40 hours at 23 °C (+/- 2 °C) and 50% R.H (+/- 5) as per ASTM standards. Standard testing conditions are 23 °C (+/- 2 °C) and 50% R.H (+/- 5) as per ASTM standards.

[00108] The test result is reported by Method A, which uses a 1.5" diameter dart head and 26" drop height. The sample thickness is measured at the sample center and the sample then clamped by an annular specimen holder with an inside diameter of 5 inches. The dart is loaded above the center of the sample and released by either a pneumatic or electromagnetic mechanism.

[00109] Testing is carried out according to the 'staircase' method. If the sample fails, a new sample is tested with the weight of the dart reduced by a known and fixed amount. If the sample does not fail, a new sample is tested with the weight of the dart increased by a known amount. After 20 specimens have been tested the number of failures is determined. If this number is 10 then the test is complete. If the number is less than 10 then the testing continues until 10 failures have been recorded. If the number is greater than 10, testing is continued until the total of non-failures is 10. The Dart drop strength is determined from these data as per ASTM D1709 and expressed in grams as the dart drop impact of Type A. All the samples analyzed were 2 mil thick.

[00110] Normalized dart is calculated by dividing the dart value by the thickness of the film.

Instrumented Dart Impact

[00111] Prior to testing the samples are conditioned for a minimum of 40hrs at 23 (+/- 2) °C and 50 (+/-10) % R.H. per ASTM D618 (Procedure A).

[00112] Instrumented dart impact is measured on a 6-inch x 6-inch square sample. The IDI dart test is based on ASTM D7192. The thickness of the film is measured at the sample center and the film is then clamped to give a 3-inch diameter unsupported test region. The film is struck by an impactor at the specimen center and perpendicular to the plane of the film. The impactor consists of a stainless-steel plunger rod 12.7 +/- 0.13 mm in diameter with a hemispherical end of the same diameter, with the end polished to a mirror finish. The impactor strikes the film specimen at 3.3 m/s with sufficient energy such that at the end of the test the reduction in speed is less than 20%. From the force versus displacement curves, peak force, energy to peak force, displacement at peak force and total displacement, and total energy are reported. Typically ten replicates are measured and the average and standard deviation of the results reported.

Melt Strength

[00113] Melt Strength testing was conducted on either Rheotester 2000 or Rheograph 25 capillary rheometers paired with a rheotens model 71.97, all of which were manufacture by Göttfert. The die used for testing has a diameter of 2mm, length of 30mm and entry angle of 180 degrees. Each test was performed isothermally at 190oC, commonly.

[00114] During the test, the sample, in pellet form, was loaded into the capillary barrel and allowed to equilibrate at the testing temperature for 10min. After which, the piston inside the barrel applies a steady force on the molten sample to achieve an apparent wall shear rate of 38.16s⁻¹, and the melt is extruded through the die with an exit velocity of approximately 9.7 mm/s. Located 100mm below the die exit, the extrudate is guided through the wheel pairs of the rheotens, which both accelerate at a constant rate of 2.4 mm/s² and measures the extrudate's response to the applied extensional force. Please note that the rheotens wheel pairs are serrated and are spaced 0.4 mm apart. The results of this testing were documented into plots of force with respect to rheotens wheel speed using the RtensEvaluations2007 excel macros. For analysis, the force at which fracture occurred in the melt is referred to as the melt strength of the material and the corresponding rheotens wheel speed at fracture is considered the drawability limit.

Gel Permeation Chromatography (GPC)

[00115] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent

Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00116] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[00117] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

[00118] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 1. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

[00119]
$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)})$$
 (EQ2)

[00120] For the determination of the viscometer and light scattering detector offsets from the IR5 detector, the Systematic Approach for the determination of multi-detector offsets is done in a manner consistent with that published by Balke, Mourey, et. al. (Mourey and Balke,

Chromatography Polym. Chpt 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, Chromatography Polym. Chpt 13, (1992)), optimizing triple detector log (MW and IV) results from a linear homopolymer polyethylene standard ($3.5 > M_w/M_n > 2.2$) with a molecular weight in the range of 115,000 to 125,000 g/mol to the narrow standard column calibration results from the narrow standards calibration curve using PolymerChar GPCOne™ Software.

[00121] The absolute molecular weight data was obtained in a manner consistent with that published by Zimm (Zimm, B.H., J. Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P., Classical Light Scattering from Polymer Solutions, Elsevier, Oxford, NY (1987)) using PolymerChar GPCOne™ software. The overall injected concentration, used in the determination of the molecular weight, was obtained from the mass detector area and the mass detector constant, derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards of known weight-average molecular weight. The calculated molecular weights (using GPCOne™) were obtained using a light scattering constant, derived from one or more of the polyethylene standards mentioned below, and a refractive index concentration coefficient, dn/dc , of -0.104. Generally, the mass detector response (IR5) and the light scattering constant (determined using GPCOne™) should be determined from a linear standard with a molecular weight in excess of about 50,000 g/mole. The viscometer calibration (determined using GPCOne™) can be accomplished using the methods described by the manufacturer, or, alternatively, by using the published values of suitable linear standards, such as Standard Reference Materials (SRM) 1475 (available from National Institute of Standards and Technology (NIST)). A viscometer constant (obtained using GPCOne™) is calculated which relates specific viscosity area (DV) and injected mass for the calibration standard to its intrinsic viscosity. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd virial coefficient effects (concentration effects on molecular weight).

[00122] The absolute weight average molecular weight ($MW_{(Abs)}$) is obtained (using GPCOne™) from the Area of the Light Scattering (LS) integrated chromatogram (factored by the light scattering constant) divided by the mass recovered from the mass constant and the mass detector (IR5) area. The molecular weight and intrinsic viscosity responses are linearly extrapolated at chromatographic ends where signal to noise becomes low (using GPCOne™). Other respective moments, $Mn_{(Abs)}$ and $Mz_{(Abs)}$ are be calculated according to equations 8-10 as follows :

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$$[00123] \quad Mn(Abs) = \frac{\sum^i IR_i}{\sum^i (IR_i / M_{Absolute_i})} \quad (EQ 3)$$

$$[00124] \quad Mw(Abs) = \frac{\sum^i IR_i \times M_{Absolute_i}}{\sum^i IR_i} \quad (EQ 4)$$

$$[00125] \quad Mz(Abs) = \frac{\sum^i (IR_i \times M_{Absolute_i}^2)}{\sum^i (IR_i \times M_{Absolute_i})} \quad (EQ 5)$$

DMS Frequency Sweep

[00126] For preparation, test samples were initially placed into a 1.5 in. diameter chase of thickness 3.10mm and compression molded at a pressure of 25,000 lbs for 6.5 min. at 190oC with a Carver Hydraulic Press (Model #4095.4NE2003). After cooling to room temperature, the sample is extracted to await rheological testing.

[00127] The DMS (dynamic mechanical spectroscopy) frequency sweep is conducted using 25mm parallel plates at frequencies ranging from 0.01 to-100 rad/s, 0.1 to 100 rad/s, and 0.1t to 500 rad/s at 150oC, 190oC, and 230oC, respectively. Test gap separating the plates is 1.8mm and a strain that satisfies linear viscoelastic conditions is utilized, typically 10% strain. Each test is conducted under nitrogen atmosphere and isothermal conditions. To initiate the DMS test, the rheometer oven is first allowed to equilibrate at the desired testing temperature for at least 30 min before loading the sample into the test geometry. The sample is then equilibrated in the oven, with the door closed, for 1 min. The test gap is then set to 1.8mm, and the sample is allotted 5 min. to relax the resulting normal force. Afterwards, the oven is quickly opened, and the sample is trimmed so that no bulge is present. The DMS measurement is then initiated after reclosing the oven. During the test, the shear elastic modulus (G'), viscous modulus (G'') and complex viscosity are measured.

[00128] All DMS frequency tests are conducted on either ARES-G2 or DHR-3 rheometers, both of which were manufactured by TA Instruments. Data analyses are conducted via TA Instruments TRIOS software.

EXAMPLES

[00129] The following examples illustrate features of the present disclosure but are not intended to limit the scope of the disclosure. The following experiments analyzed the performance of embodiments of the multilayer films described herein.

[00130] Polyethylene Compositions 1–4, which are described according to the one or more embodiments of the detailed description, were prepared by a method and utilizing the catalysts and reactors described below.

[00131] A two reactor system is used in a series configuration, as is depicted in FIG. 1. Each continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to each reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to each polymerization reactor is injected into the reactor at two locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through injection stingers. The primary catalyst component feed is computer controlled to maintain each reactor monomer conversion at the specified targets. The cocatalyst components are fed based on calculated specified molar ratios to the primary catalyst component. Immediately following each reactor feed injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of each reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around each reactor loop is provided by a pump.

[00132] In dual series reactor configuration the effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the first reactor loop and is added to the second reactor loop.

[00133] The second reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (water). At this same reactor exit location other additives are added for polymer stabilization (typical antioxidants suitable for stabilization during extrusion and film fabrication).

[00134] Following catalyst deactivation and additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The isolated polymer melt is pelletized and collected. The non-polymer stream passes through various pieces of equipment which separate most of the ethylene which is removed from the system. Most of the solvent and unreacted comonomer is recycled back to the reactor after

passing through a purification system. A small amount of solvent and comonomer is purged from the process.

[00135] The reactor stream feed data flows that correspond to the values in Table 1 used to produce the examples that are graphically described in FIG. 1. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram.

Table 1: Reactor Conditions for the Synthesis of Comparative Examples in Setup 1 (Dual Reactor)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Config.	Parallel	Parallel	Series	Series	Series	Series	Series	Series	Series	Series
Rxr 1 Temp (°C)	123	190	160	160	210	210	210	210	210	225
Rxr 1 cat	E	G	D	D	F	F	F	A	A	A
Rxr 1 Cat 1 Feed (kg/hr)	60	101	186	154	143	125	193	144	171	200
Rxr 1 Cat 1 Concentration (mmol/kg)	0.34	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Rxr 1 Cocatalyst	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A
Rxr 1 Cocatalyst equiv	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Rxr 1 Solvent Feed (kg/h)	20.58	12.53	29.8	29.7	15.51	15.51	15.51	15.83	15.83	15.83
Rxr 1 C2 Feed (kg/hr)	3.41	2.3	0.93	0.93	2.57	2.57	2.57	2.52	2.52	2.52
Rxr 1 C8 Feed (kg/hr)	1.01	0.2	0.9	0.9	1.20	1.20	1.20	1.05	1.05	1.05
Rxr 1 H2 Feed (scm)	11	11	0	4	19	19	19	4	4	4
Rxr 1 H2 Feed (mol%)	0.02	0.04	0	0.03	0.06	0.06	0.06	0.01	0.01	0.01
Rxr 1 Exit [C2] (g/L)	22.2	300	13.1	13.1	2.13	1.80	1.98	1.82	1.82	1.70
Rxr 1 solids wt%	12	15	1.7	2.1	15.6	15.6	15.6	15.6	15.6	15.6
Rxr 1 PE split wt%	60	47	11	14	40	60	60	50	50	50
Rxr 2 Temp (°C)	190	160	160	160	170	170	170	170	170	170
Rxr 2 cat	B	D	D	D	C	C	C	C	C	C
Rxr 2 Cat 1 Feed (kg/hr)	45	142	--	--	141	107	114	122.5	130	270

Rxr 2 Cat 2 Concentration (mmol/kg)	0.02	0.2	--	--	0.2	0.2	0.2	0.2	0.2	0.2
Rxr 2 Cocatalyst	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A	CoCat. A
Rxr 2 Cocatalyst equiv	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Rxr 2 Solvent Feed (kg/h)	10.03	23.4	19.3	19.6	20.18	9.00	9.00	15.59	15.59	15.49
Rxr 2 C2 Feed (kg/hr)	2.12	2.8	4.7	4.7	3.84	1.70	1.70	2.96	2.96	2.96
Rxr 2 C8 Feed (kg/hr)	0.4	1.5	0.6	0.4	0.67	0.1	0.1	0.64	0.62	0.53
Rxr 2 H2 Feed (sccm)	200	94.5	420	270	455	260	300	364	310	300
Rxr 2 H2 Feed (mol%)	0.71	0.25	0.67	0.43	0.89	1.15	1.33	0.92	0.79	0.76
Rxr 2 Exit [C2] (g/L)	4.9	12.5	13	13	3.0	2.7	3.4	2.2	2.2	1.4
Rxr 2 solids wt%	16	17	15	15	17.1	16.6	16.6	15.6	15.6	15.6
Rxr 2 PE split wt%	40	53	89	86	60	40	40	50	50	50

CoCat. A is $[\text{HN}(\text{CH}_3)(\text{C}_{18}\text{H}_{37})_2]^+[\text{B}(\text{C}_6\text{F}_5)]^-$

Table 2: Reactor Conditions for the Synthesis of Inventive Examples in Setup 1 (Dual Reactor)

Examples	Unite	1	2	3	4
Config.		Parallel	Parallel	Parallel	Parallel
Rxr 1 Temp	°C	125	125	190	190
Rxr 1 cat		E/C	E/C	I/C	I/C
Rxr 1 Cat 1 Feed	kg/hr	46	46	102	75
Rxr 1 Cat 1 Concentration	(mmol/kg)	0.34	0.34	0.2	0.4
Rxr 1 Cat 2 Feed	(kg/hr)	52	103	29	142
Rxr 1 Cat 2 Concentration	(mmol/kg)	0.2	0.2	0.08	0.04
Rxr 1 Cocatalyst		CoCat. A	CoCat. A	CoCat. A	CoCat. A
Rxr 1 Cocatalyst equiv		1.2	1.2	1.3	1.4
Rxr 1 Solvent Feed	kg/h	20.49	20.49	12.9	12.5
Rxr 1 C2 Feed	kg/h	3.41	3.41	2.3	2.2
Rxr 1 C8 Feed	kg/h	1.10	1.10	0.2	0.56
Rxr 1 H2 Feed	sccm	12	15	16	2
Rxr 1 H2 Feed	mol%	0.03	0.03	0.05	0.007
Rxr 1 Exit [C2]	g/L	20.1	20.1	3.0	3.1
Rxr 1 solids	wt%	12	12	15	15.6
Rxr 1 PE split	wt%	60	60	46	49
Rxr 2 Temp	°C	190	190		160
Rxr 2 cat		B	B	D	D
Rxr 2 Cat 1 Feed	kg/hr	0.02	0.02	152	78
Rxr 2 Cat 2 Concentration	mmol/kg	7	7	0.2	0.06
Rxr 2 Cocatalyst		CoCat. A	CoCat. A	CoCat. A	CoCat. A

Rxr 2 Cocatalyst equiv		1.2	1.2	1.2	1.3
Rxr 2 Solvent Feed	kg/h	10.11	10.03	23.9	19.4
Rxr 2 C2 Feed	kg/hr	2.09	2.12	2.8	2.8
Rxr 2 C8 Feed	kg/hr	0.4	0.4	1.5	0.97
Rxr 2 H2 Feed	sccm	198	173	94.5	104.5
Rxr 2 H2 Feed	mol%	0.71	0.61	0.25	0.28
Rxr 2 Exit [C2]	g/L	5.8	5.5	12.5	11.5
Rxr 2 solids	wt%	16	16	18	10.7
Rxr 2 PE split	wt%	40	40	54	51

Table 3. Reactor Conditions for the Synthesis of PE A, PE B, and PE C in Setup 2

Parameter	units	PE A	PE B	PE C
Reactor setup	Type	2	2	2
Comonomer type	Type	1-octene	1-octene	1-octene
First Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	7.4	5.1	5.1
First Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.590	0.265	0.266
First Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.3×10^{-4}	1.9×10^{-5}	1.9×10^{-5}
First Reactor Temperature	°C	160	190	191
First Reactor Pressure	barg	41	41	41
First Reactor Ethylene Conversion	%	85.3	80.4	80.7
First Reactor Catalyst-1 Type	Type	D	G	G
First Reactor Co-Catalyst 1 Type	Type	$[\text{HN}(\text{CH}_3)(\text{C}_{18}\text{H}_{37})_2]^+[\text{B}(\text{C}_6\text{F}_5)]^-$	MMAO-7	MMAO-7
First Reactor Co-Catalyst 2 Type	Type	MMAO-3A	None	None
First Reactor Co-Catalyst 1 to Catalyst Molar Ratio	Ratio	1.1	2750	2350
First Reactor Co-Catalyst 2 to Catalyst Molar Ratio	Ratio	10.0	--	--
First Reactor Residence Time	min	16.3	7.5	7.5
Percentage of Total Ethylene Feed to First Reactor	wt%	100	95.5	96.2
Second Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	N/A	15.6	18.8
Second Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	N/A	0.69	0.83
Second Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	N/A	0	0
Second Reactor Temperature	°C	N/A	190	190
Second Reactor Pressure	barg	N/A	42	42
Second Reactor Ethylene Conversion	%	N/A	57.4	58.5
Second Reactor Catalyst Type	Type	None	H	H
Second Reactor Co-Catalyst 1 Type	Type	None	None	None
Second Reactor Co-Catalyst 2 Type	Type	None	None	None
Second Reactor Co-Catalyst 1 to Catalyst Molar Ratio	Ratio	N/A	N/A	N/A
Second Reactor Co-Catalyst 2 to Catalyst Molar Ratio	Ratio	N/A	N/A	N/A
Second Reactor Residence Time	min	N/A	6.7	7.5

[00136] MMAO-7 is commercially available from Nouryon.

[00137] The polymers produced via the reaction conditions tabulated in Tables 1–3 were configured to a film. The films were prepared as described in the Blown Film Line Descriptions above for Lines 1 and Line 2. As indicated in Table 4 below, films were compounded from PE resins made in Continuous Reactor 2 as described in the procedure previously provided.

Table 4. Compounded Resins to Produce Inventive Examples

Example	Compounded Resin 1	Compounded Resin 2
I7	PE A	PE B
I8	PE A	PE C
I9	PE A	PE C
I10	PE A	PE C
I11	PE A	PE B
I12	PE A	PE C

Table 5: GPC Moment Averages

Example	Mn	Mw	Mz	MWD	Mn	Mw	Mz(BB)	Mz(Abs)	Mz/Mw
C1	43418	107147	232990	2.5	42336	111134	221399	235869	2.1
C2	31433	104321	191168	3.3	32692	109729	192677	193141	1.8
C17	24743	121094	506741	4.9	24128	119475	442938	416244	3.5
C18	25368	102999	261179	4.1	23725	113287	302728	370554	3.3
C19	28830	114234	272886	4.0	28755	112355	269891	257905	2.3
C20	27280	109153	276240	4.0	27986	118153	302929	394339	3.3
C21	28876	101594	219444	3.5	26011	106260	230289	260265	2.4
C22	20971	92993	211692	4.4	20747	96402	208729	216611	2.2
C23	13919	101151	491732	7.3	18574	245588	920388	5155237	21.0
C24	16098	165932	736426	10.3	21939	404266	1068837	4834301	12.0
C25	17898	148944	528675	8.3	22521	351759	860729	4322559	12.0
I1	40237	136324	1322804	3.4	40168	121457	832109	497209	4.1
I2	41755	133224	1292456	3.2	39980	118529	800164	489750	4.1
I3	20694	80548	343276	3.9	21706	81806	354422	360473	4.4
I5	23168	108822	608936	4.7	18457	109380	595590	587246	5.4
I6	24564	108531	243327	4.4	25551	108808	237882	240053	2.2
I4	24678	110617	330725	4.5	31330	116083	308439	314793	2.7
I7	40532	113356	238385	2.8	42310	123860	243768	269463	2.2
I8	39359	108364	226924	2.8	39737	118169	234476	261750	2.2
I9	39962	109889	230222	2.7	39402	120058	239596	269941	2.2
I10	40002	112665	235181	2.8	38474	120816	241189	267549	2.2
I11	41386	116882	241793	2.8	43752	127321	248181	273677	2.1
I12	42869	117034	237781	2.7	45492	127699	243488	266744	2.1

Table 6: Rheology Parameters

Example	v0.1/v100
C1	4.8
C2	3.8
C17	5.5
C18	6.8
C19	6.4
C20	8.0
C21	14.0
C22	8.5
C23	20.9
C24	49.3
C25	53.9
I1	5.5
I2	4.9
I3	4.6
I5	17.5
I6	4.5
I4	5.7
I7	8.1
I8	7.3
I9	7.6
I10	8.0
I11	8.3
I12	8.9

Table 7: Inventive Examples Compared to Single Resin PE Polymers and PE Blends

Ex.	Blown Film Line	I2 (dg/ min)	I10/ I2	Density (g/cc)	Melt Strengt h (cN)	Haze (%)	Dart Impact (g)	IDI - Total Energy (J)	Elmendorf MD Tear (gf)	Thick* (mil)	Dart** (g/mil)	Normal ized Elmen dorf MD Tear (gf/mil)
C1	2	0.86	7.1	0.924	4.4	13.7	396	0.69	730	2.0	194.0	365
C2	1	0.89	6.3	0.920	3.8	5.9	855	1.85	676	1.9	452.3	356
C11	2	0.83	9.8	0.923	12.4	7.6	652	0.72	759	2.0	324.4	380
C12	1	0.66	9.1	0.921	11.8	6.3	267	0.36	NM	2.0	131.0	NM
C13	1	0.86	8.6	0.922	8.3	2.9	309	NM	592	1.9	161.1	312
C14	2	0.86	8.3	0.923	12.5	6.2	222	0.29	545	2.0	113.3	273
C15	2	0.84	8.7	0.918	10.9	7.8	681	0.82	463	1.9	365.1	244

C16	2	0.97	8.9	0.918	7.5	6.7	789	0.89	612	1.9	415.3	322
C17	2	1.02	8.2	0.920	3.2	7.1	243	0.39	972	2.1	116.3	463
C18	2	0.97	8.5	0.916	4.1	13.5	918	2.11	652	2.1	441.3	311
C19	2	0.85	8.0	0.923	4.1	9.8	459	0.78	NM	2.2	213.0	NM
C20	2	0.85	8.5	0.926	4.9	11.8	NM	0.58	NM	2.2	NM	NM
C21	1	0.50	10.5	0.920	5.6	6.4	432	0.72	425	2.6	165.0	165
C22	1	1.00	10.1	0.920	4.7	6.0	342	0.64	488	2.6	132.6	133
C23	2	1.80	14.5	0.920	10.2	6.7	90	0.21	315	2.1	42.5	149
C24	2	0.23	17.3	0.919	21.7	30.4	79	0.26	249	2.1	37.4	118
C25	2	0.15	17.3	0.922	30.5	22.9	153	0.17	167	2.1	74.6	81.5
I1	2	0.86	7.9	0.926	10.0	15.8	NM	0.53	NM	2.0	NM	NM
I2	2	0.90	7.9	0.925	10.0	16.2	315	0.47	403	1.9	165.1	212
I3	1	0.82	7.9	0.920	9.5	10.1	918	1.62	422	2.1	428.9	201
I5	1	1.49	10.8	0.937	6.7	35.2	51	0.12	NM	2.5	20.6	NM
I6	1	0.89	6.9	0.917	5.7	4.6	852	1.76	529	2.2	381.5	240
I4	1	0.76	7.5	0.917	7.7	5.6	517	1.02	525	2.3	228.3	228
I7	2	0.78	7.7	0.921	7.5	9.8	1068	1.35	484	1.9	554.8	255
I8	2	0.63	8.2	0.921	7.9	8.9	1140	1.07	603	2.0	583.1	302
I9	2	0.61	8.5	0.920	9.7	8.9	1236	1.56	515	2.0	624.2	258
I10	2	0.56	8.4	0.918	8.3	8.4	1470	1.89	498	1.9	755.8	262
I11	2	0.51	8.2	0.916	9.3	9.4	1896	3.70	538	2.0	943.3	269
I12	2	0.50	8.1	0.917	10.4	8.7	1708	2.07	522	2.1	805.7	249

NM – Not Measured; *Thick means thickness; **Dart is Normalized Dart

[00138] The data tabulated in Table 7 indicates that the Examples I4, I7-I12 provide comparable melt strength value and better Dart A value than LDPE and LLDPE blends. As previously described, LLDPE resins are added to increase the Dart Strength of a film, however, the resins generally decrease the processability of resin. In Examples I4, I7-I12 the processability is maintained, and the dart strength is increased without the addition of LLDPE resins.

[00139] The films of Examples I4, I7-I12 have a higher melt strength and a higher dart strength than LLDPE resins (Examples C17-C20).

[00140] The Comparative Example C23-C25 resins are LDPE resins with a high molecular weight component. The high molecular weight component (approximately 10% by weight of the resin according to GPC). The high molecular weight component allows the resin to increase the physical characteristics, while maintaining the processability of the LDPE resin. The film

of Examples I4, I7-I12 have a higher dart strength than LDPE, the Comparative Example C23-C25, while the processability is only slightly less.

[00141] The comparative polymers in Table 3 are similar to the LDPE resins in the Comparative Example C23-C25 resins but without a high molecular weight component. The film of Example I4, I7-I12 have higher dart strength than LDPE, since there is no high molecular. Comparatively, the processability, melt strength is similar to the comparative polymers. Specifically Example I4, I7-I12 have melt strength of 10.4 cN, and the comparative polymers have melt strengths of 3.7, 10.4, 10.1 and 4.5 cN.

[00142] The film of Example I2 has a dart strength comparable to Comparative C19, which has a dart strength of 459 g. In contrast, the resins of Example I1 and Example I2 have much higher melt strength when compared to Comparative C19 and Comparatives C18 and C20. Example I1 has a melt strength of 10.4 cN and Example I2 has a melt strength of 10.1 cN; Comparative C19 has a melt strength of 4.1 cN; and the Comparatives C18 has a melt strength of 4.1 cN and Comparative C20 has a melt strength of 4.9 cN. The films were able to have a dart strength comparable LLDPE resins and have an increased processability.

[00143] FIG. 2 is a graph of the melt strength of the inventive examples as a function of the melt index (I2). Generally, as I2 decreases, the melt strength increases. Unexpectedly, the polymer resins have a higher-than-expected melt strength for their I2. The line drawn in the graph of FIG. 2 defined by the equation in the figure distinguishes the inventive examples, with inventive examples having melt strengths that fall above this line.

[00144] FIG. 3 is a graphical description of the normalized dart strength of the inventive examples as a function of density. Generally, as the density increases, the normalized dart strength decreases. However, the inventive examples do not correlate to the general expectation. The inventive examples have higher than expected normalized dart strength given their respective densities. The line drawn defined by the equation in the figure distinguishes the inventive examples, with inventive examples having normalized dart strength that falls above this line.

CLAIMS

1. A film comprising a polyethylene multimodal resin, wherein:
the polyethylene multimodal resin comprises the polymerized reaction product of ethylene and at least one alpha-olefin copolymer, and wherein the polyethylene multimodal resin comprises a melt strength (MS) $\geq X_1/I_2 + y$, wherein X_1 is equal to 3.9, y is equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and
wherein the film comprises a normalized dart strength (DS) greater than or equal to 9,876 minus 10,512 times the density of the polyethylene multimodal resin ($DS \geq 9,876 - 10,512 (\rho)$), wherein the normalized DS is measured in gram (g) according to ASTM 1709 Method A divided by the film thickness in mils.
2. A film comprising a polyethylene multimodal resin, wherein:
the polyethylene multimodal resin comprises the polymerized reaction product of ethylene and at least one alpha-olefin copolymer, and wherein the polyethylene multimodal resin comprises a melt strength (MS) $\geq x/I_2 + y$ wherein x is equal to 3.9, y is greater than or equal to 1.4, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C, and MS is the melt strength in cN (Rheotens device, 190°C, 2.4 mm/s², 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s⁻¹, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and
wherein the film comprises a normalized machine direction (MD) tear of greater than 190 gf/mil, wherein MD tear is measured according to ASTM D1922-15.
3. The film according to claim 1 or claim 2, wherein the film is a monolayer film.
4. The film according to any one of the preceding claims, wherein the film further comprises a layer of low density polyethylene resin having a density from 0.910 to 0.930 g/cc.
5. The film according to any one of the preceding claims, wherein the polyethylene multimodal resin comprises a density from 0.900 to 0.975 g/cc.
6. The film according to any one of the preceding claims, wherein the polyethylene multimodal resin comprises a density from 0.910 to 0.930 g/cc.

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7. The film of any preceding claim, wherein the polyethylene multimodal resin has a density greater than or equal to 0.918 g/cc, a melt strength of at least 7 cN, and a melt flow ratio (I_{10}/I_2) greater than 5, and wherein the film has a dart strength of greater than 150 g/mil.
8. The film of any preceding claim, wherein the polyethylene multimodal resin has a density from 0.910 to 0.930 g/cc, a melt strength of at least 7 cN, and a melt flow ratio (I_{10}/I_2) from 5 to 10, and wherein the film has dart strength of greater than 400 g/mil.
9. The film of any preceding claim, wherein the polyethylene multimodal resin has a melt strength of at least 7 cN, and the film has a machine direction tear of greater than 85 gf/mil as measured according to ASTM D1922-15.
10. The film of any preceding claim, wherein the polyethylene multimodal resin has a melt strength of at least 8 cN, and a rheology ratio $V_{0.1}/V_{100}$ of less than or equal to 6, and wherein the film has a dart strength of greater than 800 g, wherein $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second.
11. The film of any one of the preceding claims, wherein the polyethylene multimodal resin has an overall density of from 0.918 to 0.925 g/cc or a melt strength greater than or equal to 6 cN.