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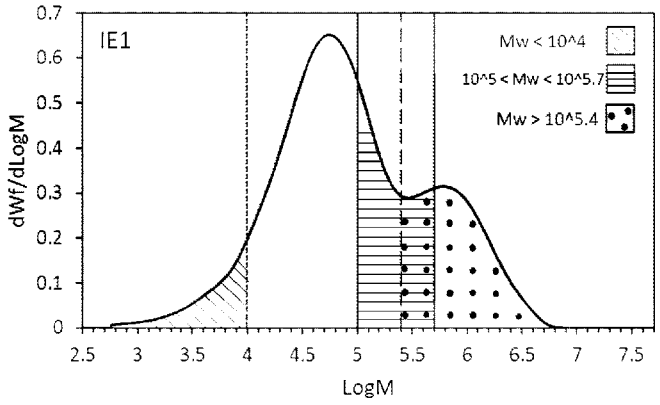
(54) Title: MULTIMODAL POLYETHYLENE COMPOSITIONS

FIGURE 1



(57) **Abstract:** Provided are multimodal polyethylene compositions and blow molded articles made from the same. The multimodal polyethylene composition according to embodiments disclosed herein have a density of from 0.935 g/cm^3 to 0.980 g/cm^3 and a certain molecular weight distribution as shown in a chromatogram characterized by absolute GPC. The multimodal polyethylene composition is suitable for blow molding application and can deliver a balance between melt strength, impact resistance, and ESCR properties.

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MULTIMODAL POLYETHYLENE COMPOSITIONS

TECHNICAL FIELD

[0001] Embodiments of the present disclosure generally relate to multimodal polyethylene compositions, and blow molded articles including the same.

INTRODUCTION

[0002] Polyethylene compositions can be formed into useful articles via blow molding. Blow molding can produce articles such a bottles, containers, automotive components, gas tanks, and drums. The articles require a combination of processability and mechanical properties, including melt strength, impact resistance, and environmental stress crack resistance, to meet performance criteria and longevity in real-world applications. Conventional polyethylene compositions used for blow molding include chromium catalyzed resins with unimodal designs exhibiting high melt strength with relatively poor impact resistance and environmental stress crack resistance (ESCR), as well as multimodal metallocene and Ziegler-Natta catalyzed designs exhibiting less desirable melt strength but better impact resistance and ESCR. High melt strength in blow molding prevents material from sagging under the influence of heat and pressure, but the trade-off between melt strength and other properties such as impact resistance and ESCR poses significant challenges. Articles must not only maintain their structural integrity during the molding process but also exhibit enhanced toughness and resistance to environmental stresses after molding.

[0003] Accordingly, there is a need for multimodal polyethylene compositions suitable for use in blow molding applications that delivers a balance between melt strength, impact resistance, and ESCR properties.

SUMMARY

[0004] Embodiments of the present disclosure meet one or more of the foregoing needs by providing a polyethylene composition that can be produced in a single reactor and can achieve desirable processability, melt strength, impact resistance, and ESCR for blow molding application.

[0005] Disclosed herein is a multimodal polyethylene composition. In one aspect, the multimodal polyethylene composition has a density of from 0.935 g/cm^3 to 0.980 g/cm^3,

wherein the multimodal polyethylene composition has a molecular weight distribution as shown in a chromatogram characterized by absolute GPC as follows: a) a first absolute GPC fraction of less than 10,000 Daltons less than 10.0%; b) a second absolute GPC fraction of from $10^{5.0}$ to $10^{5.7}$ Daltons between 20.0 to 40.0%; and c) a third absolute GPC fraction of greater than $10^{5.4}$ Daltons greater than 25.5%, wherein percent (%) is based on percent area under the curve shown in the chromatogram characterized by absolute GPC.

[0006] Disclosed herein is a blow molding process. In this aspect, the bold molding process comprises the steps of: (1) placing a quantity of molten polyethylene in a mold cavity, (2) blowing a gas into the molten polyethylene, causing it to expand and assume the approximate shape of the mold cavity, and (3) cooling the molten polyethylene, wherein the molten polyethylene is the multimodal polyethylene composition according to the first aspect of the invention.

[0007] Disclosed herein is a blow molded article. In this aspect, the blow molded article comprises the multimodal polyethylene composition according to the first aspect of the invention.

[0008] These and other embodiments are described in more detail in the Detailed Description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1-3 depict a GPC chromatogram of an example according to the embodiments disclosed herein.

DETAILED DESCRIPTION

[0010] Aspects of the disclosed multimodal polyethylene compositions are described in more detail below. The multimodal polyethylene compositions are suitable for use in forming blow molded articles and in particular large part blow molded articles, where a balance of melt strength, impact resistance, and ESCR is critical. The multimodal polyethylene compositions formed into blow molded articles can have a wide variety of applications, including, for example, large containers, automotive components, gas tanks, and drums.

[0011] As used herein, the term "polymer" means a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer

thus embraces the term homopolymer (employed to refer to polymers prepared from only one type of monomer), and the term copolymer or interpolymer. Trace amounts of impurities (for example, catalyst residues) may be incorporated into and/or within the polymer. A polymer may be a single polymer, a polymer blend, or a polymer mixture, including mixtures of polymers that are formed *in situ* during polymerization.

[0012] As used herein, the term "copolymer" means a polymer formed by the polymerization reaction of at least two structurally different monomers. The term "copolymer" is inclusive of terpolymers.

[0013] As used herein, the terms "polyethylene" or "ethylene-based polymer" shall mean polymers comprising a majority amount (>50 mol %) of units which have been derived from ethylene monomer. This includes polyethylene homopolymers and copolymers (meaning units derived from two or more comonomers). The terms "ethylene-based polymer" and "polyethylene" may be used interchangeably. Generally, polyethylene may be produced in gas-phase, fluidized bed reactors, liquid phase slurry process reactors, or liquid phase solution process reactors, using a heterogeneous catalyst system, such as Ziegler-Natta catalyst, a homogeneous catalyst system, comprising Group 4 transition metals and ligand structures such as metallocene, non-metallocene metal-centered, heteroaryl, heterovalent aryloxyether, phosphinimine, and others. Combinations of heterogeneous and/or homogeneous catalysts also may be used in either single reactor or dual reactor configurations.

[0014] As used herein, the term "composition" refers to a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[0015] The term "multimodal" means compositions that can be characterized by having at least two (2) polyethylene components or subcomponents with different molecular weights and/or different comonomer contents. The term "bimodal" means compositions that can be characterized by having two (2) polyethylene components or subcomponents with different molecular weights and/or different comonomer contents. All GPC measurement values (e.g., Mw, Mn, Mz) recited herein are Absolute GPC measurements provided in accordance with the test methods described below.

[0016] 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.

[0017] Disclosed herein are multimodal polyethylene compositions. The multimodal polyethylene composition according to embodiments disclosed herein has a density of from 0.935 g/cm^3 to 0.980 g/cm^3. All individual values and subranges of from 0.935 g/cm^3 to 0.980 g/cm^3 are disclosed and incorporated herein. For example, the multimodal polyethylene composition can have a density lower limit from 0.935, 0.940, 0.945, 0.950, 0.955, 0.960, 0.965, 0.970 or 0.975 g/cm^3 to an upper limit from 0.980, 0.975, 0.970, 0.965, 0.960, 0.955, 0.950, 0.945, or 0.940 g/cm^3. In some embodiments, the multimodal polyethylene composition has a density from 0.950 to 0.960 g/cm^3.

[0018] The multimodal polyethylene composition has a molecular weight distribution as shown in a chromatogram characterized by absolute GPC as follows: a first absolute GPC fraction of less than 10,000 Daltons less than 10.0%; a second absolute GPC fraction of from $10^{5.0}$ to $10^{5.7}$ Daltons between 20.0 to 40.0%; and a third absolute GPC fraction of greater than $10^{5.4}$ Daltons greater than 25.5%; wherein percent (%) is based on percent area under the curve shown in the chromatogram characterized by absolute GPC. The absolute GPC fractions of the multimodal polyethylene composition can be measured in accordance with the test method described below. Without being bound by theory, it has been found that the unique GPC chromatogram with specified GPC fractions according to embodiments described herein contributes to polyethylene compositions having excellent processability as well as a desirable balance of melt strength, ESCR, and impact resistance suitable for blow molding applications.

[0019] In some embodiments, the first absolute GPC fraction of less than 10,000 Daltons is less than 9.0% or less than 8.0%. In some embodiments, the first absolute GPC fraction of less than 10,000 Daltons is greater than 1.0% or greater than 2.0%, or greater than 3.0%, or greater than 4.0%, or greater than 5.0%, or between 1.0 to 10.0%, between 2.0 to 10.0%, between 3.0 to 10.0 %, or between 4.0 to 10.0 %, or between 5.0 to 10.0%.

[0020] In some embodiments, the second absolute GPC fraction of from $10^{5.0}$ to $10^{5.7}$ Daltons is between a lower limit of 20.0, or 21.0, or 22.0, or 23.0 % to an upper limit of 40.0, or 38.0, or 36.0, or 34.0, or 32.0, or 30.0, or 28.0, or 26.0 or 25.0 %. In some embodiments, the third absolute GPC fraction of greater than $10^{5.4}$ Daltons greater than 25.5%, or greater than 26.0 %, or in the range of from 25.5 to 32.0%, or from 25.5 to 30.0%.

[0021] In some embodiments, in addition to being characterized by the GPC fractions, the multimodal polyethylene compositions comprise a first polyethylene component and a second polyethylene component. In some embodiments, the multimodal composition is a bimodal polyethylene composition (i.e., it has only two polyethylene components). In some embodiments, the multimodal composition is a trimodal polyethylene composition and comprises a first, second, and third polyethylene component. In other embodiments, the multimodal composition has two, three, or more polyethylene components with different molecular weights and/or different comonomer contents.

[0022] In some embodiments, the first polyethylene component is a copolymer of ethylene and one or more alpha-olefin comonomers. In some embodiments, the second polyethylene component is also a copolymer of ethylene and one or more alpha-olefin comonomers. The alpha-olefin comonomers can have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary alpha-olefin comonomers 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. In some embodiments, the alpha-olefin comonomers may be selected from the group consisting of 1-butene, 1-hexene, and 1-octene, or from the group consisting of 1-butene and 1-hexene, or from the group consisting of 1-hexene and 1-octene. In some embodiments, the first polyethylene component is a non-metallocene catalyzed ethylene copolymer. In some embodiments, the second polyethylene component is a metallocene catalyzed ethylene copolymer. As discussed below, the first polyethylene component and the second polyethylene component can be polymerized in a single reactor in the presence of bimodal catalyst system. In some embodiments, the first polyethylene component is a copolymer comprising ethylene and 1-hexene. In some embodiments, the second polyethylene component is a copolymer comprising ethylene and 1-hexene. In some embodiments, the first polyethylene component and second polyethylene component comprise 1-hexene or are void of comonomers other than 1-hexene, or void of comonomers other 1-hexene or 1-octene.

[0023] The multimodal polyethylene composition has a high flow melt index (I_{21}) of from 4.0 to 7.0 g/10 min. In some embodiments, multimodal polyethylene composition can have a high flow melt index (I_{21}) of from a lower limit of 4.0, 4.5, 5.0, 5.2, to an upper limit of 7.0, 6.5, 6.4, or 6.0 g/10 min.

[0024] In some embodiments, the multimodal polyethylene composition has an I_5 of 0.10 to 0.50 g/10 min, or 0.10 to 0.40 g/10 min, or 0.10 to 0.30 g/10 min, or 0.10 to 0.25 g/10 min, or 0.10 to 0.20 g/10 min. In some embodiments, the multimodal polyethylene composition can have a I_{21}/I_5 in the range of from 30 to 60, or from 30 to 55, or from 35 to 55, or from 36 to 50.

[0025] In some embodiments, the multimodal polyethylene composition has a number average molecular weight (Mn) of less than 40,000 Dalton, or less than 38,000 Dalton, or less than 37,000 Dalton. In some embodiments, the multimodal polyethylene composition has a weight average molecular weight (Mw) of greater than 250,000 Dalton, or greater than 275,000 Dalton, or greater than 300,000 Dalton, or greater than 310,000 Dalton. In some embodiments, the multimodal polyethylene composition has an Mz of greater than 1,000,000 Dalton, or greater than 1,100,000 Dalton, or greater than 1,200,000 Dalton, or greater than 1,300,000 Dalton, or greater than 1,400,000 Dalton, or greater than 1,500,000 Dalton. The GPC measurements of Mw, Mn, and Mz are measured in accordance with the test method described below.

[0026] In some embodiments, the multimodal polyethylene composition has at least one of the following: an environmental stress cracking resistance (ESCR) greater than 500 hours; a Charpy Impact value of greater than 40 kJ/m^2; a melt strength of greater than 15.0 centinewtons (cN); or a 1% secant flexural modulus (0.5 in/min) of greater than 155 ksi. In some embodiments, the multimodal polyethylene composition has an ESCR of greater than 600 hours. In some embodiments, the multimodal polyethylene composition has a Charpy Impact value of greater than 40 kJ/m^2 or greater than 45 kJ/m^2, or greater than 50 kJ/m^2. In some embodiments, the multimodal polyethylene composition has a melt strength of greater than 16.0, or greater than 17.0 cN. In some embodiments, the multimodal polyethylene composition has a 1% secant flexural modulus (0.5 in/min) of greater than 155 ksi, or greater than 160 ksi, or greater than 165 ksi, or greater than 170 ksi.

[0027] In some embodiments, the multimodal polyethylene composition can have a molecular weight distribution from Absolute GPC, where the Absolute GPC molecular weight

distribution has a first peak and a second peak in a range of Log(molecular weight) of 3.5 to 7.0, wherein the first peak corresponds to the second polyethylene component and the second peak corresponds to the first polyethylene component. Figure 1 discloses a GPC chromatogram displaying a first peak and a second peak, as well as the three GPC fractions. A person of ordinary skill in the art understands that the GPC chromatogram relates to the molecular architecture of the multimodal polyethylene composition and is in part a result of the particular catalyst system used to form the composition. Without being bound by theory, it has been found that, according to embodiments disclosed herein, a particular type of catalyst and process conditions are suitable for producing the multimodal polyethylene composition in a single reactor and, relatedly, delivering a specific GPC chromatogram, whereas prior art compositions with similar features or different catalyst systems cannot be made in a single reactor system, deliver the specific GPC chromatogram, and/or deliver the desirable properties disclosed herein.

[0028] The multimodal polyethylene composition of the present invention is suitable for forming blow molded articles, although articles can also be formed by other processes known to those skilled in the art such as injection molding or rotomolding. A blow molding process may comprise the steps of: (1) placing a quantity of molten polyethylene in a mold cavity, (2) blowing a gas into the molten polyethylene, causing it to expand and assume the approximate shape of the mold cavity, and (3) cooling the molten polyethylene, wherein the molten polyethylene is the multimodal polyethylene composition according to embodiments disclosed herein.

[0029] The blow molded articles according to embodiments disclosed herein may be a monolayer article and may comprise suitable additives used for blow molding applications. Such additives include colorants and materials suitable to protect the composition from adverse environmental effect, for example, oxidation during extrusion or degradation under service conditions. Suitable additives include process stabilizers, antioxidants, and pigments. In some embodiments, the articles may comprise multiple layers wherein at least one layer comprises the composition according to the present invention. Additional polyolefins may be coextruded with other polymers such as polyethylene, polypropylene, polyamides, ethylene vinyl alcohol copolymers and polyesters.

Process for Making the Multimodal Composition

[0030] In some embodiments, the multimodal polyethylene composition is made by the process of polymerizing ethylene and an alpha-olefin comonomer in the presence of a bimodal catalyst system in a single gas phase polymerization (GPP). In some embodiments, the multimodal polyethylene composition can be prepared by polymerizing ethylene and an alpha-olefin in the presence of a bimodal catalyst system in a single gas phase polymerization (GPP); wherein the bimodal catalyst system consists essentially of a metallocene catalyst, a single-site non-metallocene catalyst that is a bis((alkyl-substituted phenylamido)ethyl)amine catalyst, optionally a host material, and optionally an activator; wherein the host material, when present, is selected from at least one of an inert hydrocarbon liquid and a solid support; wherein the metallocene catalyst is an activation reaction product of contacting an activator with a metal-ligand complex of formula $(R_{1-2}Cp)((alkyl)_{1-3}Indenyl)MX_2$, wherein R is hydrogen, methyl, or ethyl; each alkyl independently is a $(C_1\text{-}C_4)$alkyl; M is titanium, zirconium, or hafnium; and each X is independently a halide, a $(C_1$ to $C_{20})$alkyl, a $(C_7$ to $C_{20})$aralkyl, a $(C_1$ to $C_6)$alkyl-substituted $(C_6$ to $C_{12})$aryl, or a $(C_1$ to $C_6)$alkyl-substituted benzyl; and wherein the bis((alkyl-substituted phenylamido)ethyl)amine catalyst is an activation reaction product of contacting an activator with a bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2, wherein each R^1 is independently selected from F, Cl, Br, I, benzyl, $-CH_2Si(CH_3)_3$, a $(C_1\text{-}C_5)$alkyl, and a $(C_2\text{-}C_5)$alkenyl.

[0031] In some embodiments, the multimodal polyethylene composition is made by polymerizing ethylene and an alpha-olefin in the presence of a bimodal catalyst system in a single gas phase polymerization (GPP); wherein the H2/C2 and process conditions are controlled in the GPP comprising the bimodal catalyst system consisting essentially of a metallocene catalyst, a single-site non-metallocene catalyst that is a bis((alkyl-substituted phenylamido)ethyl)amine catalyst, optionally a host material, and optionally an activator; wherein the host material, when present, is selected from at least one of an inert hydrocarbon liquid and a solid support; wherein the metallocene catalyst is an activation reaction product of contacting an activator with a metal-ligand complex of formula $(R_{1-2}Cp)((alkyl)_{1-3}Indenyl)MX_2$, wherein R is hydrogen, methyl, or ethyl; each alkyl independently is a $(C_1\text{-}C_4)$alkyl; M is titanium, zirconium, or hafnium; and each X is independently a halide, a $(C_1$ to $C_{20})$alkyl, a $(C_7$ to $C_{20})$aralkyl, a $(C_1$ to $C_6)$alkyl-substituted $(C_6$ to $C_{12})$aryl, or a $(C_1$ to $C_6)$alkyl-

substituted benzyl; and wherein the bis((alkyl-substituted phenylamido)ethyl)amine catalyst is an activation reaction product of contacting an activator with a bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2, wherein each R^1 is independently selected from F, Cl, Br, I, benzyl, $-CH_2Si(CH_3)_3$, a (C_1-C_5)alkyl, and a (C_2-C_5)alkenyl.

[0032] In some embodiments, the multimodal polyethylene composition may be a polymerized reaction product of an ethylene monomer and at least one C_3-C_{12} alpha-olefin comonomer. For example, embodiments of the composition may be a polymerized reaction product of an ethylene monomer and 1-butene, 1-hexene, or both. Alternatively, embodiments of the polyethylene composition may be a polymerized reaction product of an ethylene monomer and 1-butene, 1-octene, or both. Embodiments of the polyethylene composition may also be a polymerized reaction product of an ethylene monomer and 1-hexene, 1-octene, or both. In some embodiments, the C_3-C_{12} alpha-olefin comonomer may not be propylene.

[0033] In some embodiments, the multimodal polyethylene composition may be produced with a catalyst system in a single reactor. As used herein, a "catalyst system" may comprise a main catalyst, a trim catalyst, and, optionally, at least one activator. Catalyst systems may also include other components, such as supports, and are not limited to a main catalyst, a trim catalyst, and, optionally, at least one activator. Embodiments of the catalyst system may comprise a main catalyst and a metallocene trim catalyst. Embodiments of the catalyst system may also comprise one or more additives commonly used in the art of olefin polymerization. For example, embodiments of the catalyst system may comprise one or more continuity additives, flow aids, and anti-static aids. In embodiments, the reactor may be a gas phase reactor, although slurry phase reactors may also be used.

[0034] Embodiments of the catalyst system may comprise at least one catalyst for producing the first polyethylene component (a higher molecular weight component) by polymerization (sometimes referred to herein as an "HMW catalyst"), and at least one catalyst compound for producing the second polyethylene component (a lower molecular weight component) by polymerization (sometimes referred to herein as an "LMW catalyst").

[0035] Embodiments of the catalyst system may be referred to as a "bimodal catalyst system." Such a catalyst system produces a polyethylene composition having separate, identifiable high molecular weight and low molecular weight distributions. The term "bimodal catalyst system" may comprise any formulation, mixture, or system that comprises at least two

different catalyst compounds, each having the same or a different metal group, but generally different ligands or catalyst structure, including a "dual catalyst." Alternatively, each different catalyst compound of the bimodal catalyst system resides on a single support particle, in which case a dual catalyst is considered to be a supported catalyst. However, the term "bimodal catalyst system" also broadly comprises a system or mixture in which one of the catalysts resides on one collection of support particles, and another catalyst resides on another collection of support particles. In such embodiments, the two supported catalysts are introduced to a single reactor, either simultaneously or sequentially, and polymerization is conducted in the presence of the two collections of supported catalysts. Alternatively, the bimodal catalyst system may comprise a mixture of unsupported catalysts in slurry form.

[0036] The single gas phase polymerization reactor may be a fluidized-bed gas phase polymerization (FB-GPP) reactor and the effective polymerization conditions may comprise conditions (a) to (e): (a) the FB-GPP reactor having a fluidized resin bed at a bed temperature from 60 to 120 degrees Celsius (°C), alternatively from 70 to 115°C, alternatively from 75 to 110°C, alternatively from 77 to 107°C, alternatively from 80°C to 95°C; (b) the FB-GPP reactor receiving feeds of respective independently controlled amounts of ethylene, 1-alkene characterized by a 1-alkene-to-ethylene (C_X/C_2) molar ratio, the bimodal catalyst system, optionally a trim catalyst comprising a solution in an inert hydrocarbon liquid of a dissolved amount of unsupported form of the metallocene catalyst made from the metal-ligand complex of formula (I) and activator, optionally hydrogen gas (H_2) characterized by a hydrogen-to-ethylene (H_2/C_2) molar ratio or by a weight parts per million H_2 to mole percent C_2 ratio (H_2 ppm/C_2 mol%), and optionally an induced condensing agent (ICA) comprising a (C_5-C_{10})alkane(s), e.g., isopentane; wherein the (C_6/C_2) molar ratio is from 0.0001 to 0.1, alternatively from 0.0002 to 0.03, alternately from 0.003 to 0.02; wherein when H_2 is fed, the H_2/C_2 molar ratio is from 0.0001 to 0.1, alternatively from 0.0002 to 0.0020, alternately from 0.0003 to 0.001, or the H_2 ppm/C_2 mol% ratio is from 1 to 1,000, alternatively from 2.0 to 20.0, alternately from 3.0 to 10.0; and wherein when the ICA is fed, the concentration of ICA in the reactor is from 1 to 25 mole percent (mol%), alternatively from 4 to 20 mol%, based on total moles of ethylene, 1-alkene, inerts and ICA in the reactor. The average residence time of the copolymer in the reactor may be from 1 to 6 hours, alternatively from 2 to 4 hours. A continuity additive may be used in the FB-GPP reactor during polymerization.

[0037] The bimodal catalyst system may be characterized by an inverse response to bed temperature such that when the bed temperature is increased, the viscoelastic property value of the resulting composition is decreased, and when the bed temperature is decreased, the viscoelastic property value of the resulting bimodal poly(ethylene-*co*-1-alkene) copolymer is increased. The bimodal catalyst system may be characterized by an inverse response to the H_2/C_2 ratio such that when the H_2/C_2 ratio is increased, the viscoelastic property value of the resulting bimodal poly(ethylene-*co*-1-alkene) copolymer is decreased, and when the H_2/C_2 ratio is decreased, the viscoelastic property value of the resulting composition is increased.

[0038] The composition comprises the higher molecular weight component (HMW component) and the lower molecular weight component (LMW component). In an illustrative pilot plant process for making the bimodal polyethylene polymer, a fluidized bed, gas-phase polymerization reactor ("FB-GPP reactor") having a reaction zone dimensioned as 304.8 mm (twelve inch) internal diameter and a 2.4384 meter (8 feet) in straight-side height and containing a fluidized bed of granules of the composition. Configure the FB-GPP reactor with a recycle gas line for flowing a recycle gas stream. Fit the FB-GPP reactor with gas feed inlets and polymer product outlet. Introduce gaseous feed streams of ethylene and hydrogen together with 1-alkene comonomer (e.g., 1-hexene) below the FB-GPP reactor bed into the recycle gas line. Measure the (C_5-C_{20})alkane(s) total concentration in the gas/vapor effluent by sampling the gas/vapor effluent in the recycle gas line. Return the gas/vapor effluent (other than a small portion removed for sampling) to the FB-GPP reactor via the recycle gas line.

[0039] Polymerization operating conditions are any variable or combination of variables that may affect a polymerization reaction in the GPP reactor or a composition or property of a bimodal polyethylene copolymer made thereby. The variables may include reactor design and size, catalyst composition and amount; reactant composition and amount; molar ratio of two different reactants; presence or absence of feed gases such as H_2 and/or O_2, molar ratio of feed gases versus reactants, absence or concentration of interfering materials (e.g., H_2O), average polymer residence time in the reactor, partial pressures of constituents, feed rates of monomers, reactor bed temperature (e.g., fluidized bed temperature), nature or sequence of process steps, time periods for transitioning between steps. Variables other than that/those being described or changed by the method or use may be kept constant.

[0040] In operating the method, control individual flow rates of ethylene ("C_2"), 1-alkene ("C_X", e.g., 1-hexene or "C_6" or "C_X" wherein x is 6), and any hydrogen ("H_2") to maintain a fixed comonomer to ethylene monomer gas molar ratio (C_X/C_2, e.g., C_6/C_2) equal to a described value, a constant hydrogen to ethylene gas molar ratio ("H_2/C_2") equal to a described value, and a constant ethylene ("C_2") partial pressure equal to a described value (e.g., 1,000 kPa). Alternately, individual flow rates of ethylene ("C_2"), 1-alkene ("C_X", e.g., 1-hexene or "C_6" or "C_X" wherein x is 6), and any hydrogen ("H_2") to maintain a fixed comonomer to ethylene monomer gas flow ratio (C_X/C_2 flow ratio, e.g., kg C_6/kg C_2 FR) equal to a described value, a constant hydrogen to ethylene gas flow ratio ("H_2/C_2 flow ratio" e.g., kg H_2/kg C_2 FR) equal to a described value, and a constant ethylene ("C_2") partial pressure equal to a described value (e.g., 1,000 kPa). Measure concentrations of gases by an in-line gas chromatograph to understand and maintain composition in the recycle gas stream. Maintain a reacting bed of growing polymer particles in a fluidized state by continuously flowing a make-up feed and recycle gas through the reaction zone. Use a superficial gas velocity of 0.43 to 0.76 meter per second (m/sec) (1.4 to 2.5 feet per second (ft/sec)). Operate the FB-GPP reactor at a total pressure of about 2000 to about 2413 kilopascals (kPa) (about 290 to about 350 pounds per square inch-gauge (psig)) and at a described reactor bed temperature RBT. Maintain the fluidized bed at a constant height by withdrawing a portion of the bed at a rate equal to the rate of production of particulate form of the bimodal polyethylene polymer, which production rate may be from 4,500 to 90,000 kilograms per hour (kg/hr), alternatively 9,000 to 80,000 kg/hr. Remove the produced bimodal poly(ethylene-*co*-1-alkene) copolymer semi-continuously via a series of valves into one or more fixed volume chambers, convey the resin to a product purge bin and contact the removed composition stepwise with a suitable purging medium to remove solubilized hydrocarbons and then contact the resin with a stream of humidified nitrogen (N_2) gas to deactivate any trace quantities of residual catalysts.

[0041] The bimodal catalyst system may be fed into the polymerization reactor(s) in "dry mode" or "wet mode", alternatively dry mode, alternatively wet mode. The dry mode is a dry powder or granules. The wet mode is a suspension in an inert liquid such as mineral oil or the (C_5-C_{20})alkane(s). In some aspects the composition is made by contacting the metal-ligand complex of formula (I) and the single-site non-metallocene catalyst with at least one activator *in situ* in the GPP reactor in the presence of olefin monomer and comonomer (e.g., ethylene

and 1-alkene) and growing polymer chains. These embodiments may be referred to herein as *in situ*-contacting embodiments. In other aspects the metal-ligand complex of formula (I), the single-site non-metallocene catalyst, and the at least one activator are pre-mixed together for a period of time to make an activated bimodal catalyst system, and then the activated bimodal catalyst system is injected into the GPP reactor, where it contacts the olefin monomer and growing polymer chains. These latter embodiments pre-contact the metal-ligand complex of formula (I), the single-site non-metallocene catalyst, and the at least one activator together in the absence of olefin monomer (e.g., in absence of ethylene and alpha-olefin) and growing polymer chains, i.e., in an inert environment, and are referred to herein as pre-contacting embodiments. The pre-mixing period of time of the pre-contacting embodiments may be from 1 second to 10 minutes, alternatively from 30 seconds to 45 minutes, alternatively from 5 minutes to 30 minutes. The ICA may be fed separately into the FB-GPP reactor or as part of a mixture also containing the bimodal catalyst system. The ICA may be a (C_{11}-C_{20}) alkane, alternatively a (C_5-C_{10})alkane, alternatively a (C_5)alkane, e.g., pentane or 2-methylbutane; a hexane; a heptane; an octane; a nonane; a decane; or a combination of any two or more thereof. The aspects of the polymerization method that use the ICA may be referred to as being an induced condensing mode operation (ICMO). ICMO is described in US 4,453,399; US 4,588,790; US 4,994,534; US 5,352,749; US 5,462,999; and US 6,489,408. The concentration of ICA in the reactor is measured indirectly as total concentration of vented ICA in recycle line using gas chromatography by calibrating peak area percent to mole percent (mol%) with a gas mixture standard of known concentrations of ad rem gas phase components.

[0042] The method uses a gas-phase polymerization (GPP) reactor, such as a stirred-bed gas phase polymerization reactor (SB-GPP reactor) or a fluidized-bed gas-phase polymerization reactor (FB-GPP reactor), to make the composition disclosed herein. Such gas phase polymerization reactors and methods are generally well-known in the art. For example, the FB-GPP reactor/method may be as described in US 3,709,853; US 4,003,712; US 4,011,382; US 4,302,566; US 4,543,399; US 4,882,400; US 5,352,749; US 5,541,270; EP-A-0 802 202; and Belgian Patent No. 839,380. These SB-GPP and FB-GPP polymerization reactors and processes either mechanically agitate or fluidize by continuous flow of gaseous monomer and diluent the polymerization medium inside the reactor, respectively. Other useful reactors/processes contemplated include series or multistage polymerization processes such as described in US 5,627,242; US 5,665,818; US 5,677,375; EP-A-0 794 200; EP-B1-0 649 992; EP-A-0 802 202; and EP-B-634421.

[0043] The polymerization conditions may further include one or more additives such as a chain transfer agent or a promoter. The chain transfer agents are well known and may be alkyl metal such as diethyl zinc. Promoters are known such as in US 4,988,783 and may include chloroform, $CFCl_3$, trichloroethane, and difluorotetrachloroethane. Prior to reactor start up, a scavenging agent may be used to react with moisture and during reactor transitions a scavenging agent may be used to react with excess activator. Scavenging agents may be a trialkylaluminum. Gas phase polymerizations may be operated free of (not deliberately added) scavenging agents. The polymerization conditions for gas phase polymerization reactor/method may further include an amount (e.g., 0.5 to 200 ppm based on all feeds into reactor) of a static control agent and/or a continuity additive such as aluminum stearate or polyethyleneimine. The static control agent may be added to the FB-GPP reactor to inhibit formation or buildup of static charge therein. The static control agent may be added to the FB-GPP reactor prior at a preset concentration prior to initiating the catalyst feed.

[0044] The method may use a fluidized bed gas phase polymerization reactor FB-GPP that comprises a reactor vessel containing a fluidized bed of a powder of the bimodal polyethylene polymer, and a distributor plate disposed above a bottom head, and defining a bottom gas inlet, and having an expanded section, or cyclone system, at the top of the reactor vessel to decrease amount of resin fines that may escape from the fluidized bed. The expanded section defines a gas outlet. The FB-GPP further comprises a compressor blower of sufficient power to continuously cycle or loop gas around from out of the gas outlet in the expanded section in the top of the reactor vessel down to and into the bottom gas inlet of the FB-GPP and through the distributor plate and fluidized bed. The FB-GPP further comprises a cooling system to remove heat of polymerization and maintain the fluidized bed at a target temperature. Compositions of gases such as ethylene, 1-alkene (e.g., 1-hexene), and hydrogen being fed into the Pilot Reactor are monitored by an in-line gas chromatograph in the cycle loop in order to maintain specific concentrations thereof that define and enable control of polymer properties. The bimodal catalyst system may be fed as a slurry or dry powder into the FB-GPP from high pressure devices, wherein the slurry is fed via a pump and the dry powder is fed via a metered disk. The bimodal catalyst system typically enters the fluidized bed in the lower 1/3 of its bed height. The FB-GPP further comprises a way of monitoring the weight of the fluidized bed and isolation ports (Product Discharge System) for discharging the powder of bimodal polyethylene polymer from the reactor vessel in response to an increase of the fluidized bed weight as polymerization reaction proceeds.

[0045] In some embodiments the FB-GPP reactor is a commercial scale reactor such as a UNIPOL™ reactor, which is available from Univation Technologies, LLC, a subsidiary of The Dow Chemical Company, Midland, Michigan, USA. In some embodiments, the bimodal catalyst system used in the method consists essentially of the metallocene catalyst and the bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2 catalyst, and, optionally, the host material; wherein the host material, when present, is selected from the at least one of the inert hydrocarbon liquid and the solid support; wherein the metallocene catalyst is an activation reaction product of contacting an activator with a metal-ligand complex of formula (I) described earlier; and wherein the bis((alkyl-substituted phenylamido)ethyl)amine catalyst is an activation reaction product of contacting an activator with the bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2 catalyst described earlier. The phrase consists essentially of means that the bimodal catalyst system and method using same is free of a third single-site catalyst (e.g., a different metallocene, a different amine catalyst, or a biphenylphenolic catalyst) and free of non-single site catalysts (e.g., free of Ziegler-Natta or chromium catalysts). The bimodal catalyst system may also consist essentially of the host material and/or at least one activator species, which is a by-product of reacting the metallocene catalyst or non-metallocene molecular catalyst with the activator(s).

[0046] Without being bound by theory, it is believed that the bis((alkyl-substituted phenylamido)ethyl)amine catalyst (e.g., the bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl) is a substantially single-site non-metallocene catalyst that is effective for making the HMW component of the bimodal poly(ethylene-*co*-1-alkene) copolymer and the metallocene catalyst (made from the metal-ligand complex of formula (I)) is a substantially single-site catalyst that is independently effective for making the LMW component of the composition. The molar ratio of the two catalysts of the bimodal catalyst system may be based on the molar ratio of their respective catalytic metal atom (M, e.g., Zr) contents, which may be calculated from ingredient weights thereof or may be analytically measured. The molar ratio of the two catalysts may be varied in the polymerization method by way of using a different bimodal catalyst system formulation having different molar ratio thereof or by using a same bimodal catalyst system and the trim catalyst. Varying the molar ratio of the two catalysts during the polymerization method may be used to vary the particular properties of the bimodal poly(ethylene-*co*-1-alkene) copolymer within the limits of the described features thereof.

[0047] The catalysts of the bimodal catalyst system may be unsupported when contacted with an activator, which may be the same or different for the different catalysts. Alternatively, the catalysts may be disposed by spray-drying onto a solid support material prior to being contacted with the activator(s). The solid support material may be uncalcined or calcined prior to being contacted with the catalysts. The solid support material may be a hydrophobic fumed silica (e.g., a fumed silica treated with dimethyldichlorosilane). The bimodal (unsupported or supported) catalyst system may be in the form of a powdery, free-flowing particulate solid. Support material. The support material may be an inorganic oxide material. The terms "support" and "support material" are the same as used herein and refer to a porous inorganic substance or organic substance. In some embodiments, desirable support materials may be inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 oxides, alternatively Group 13 or 14 atoms. Examples of inorganic oxide-type support materials are silica, alumina, titania, zirconia, thoria, and mixtures of any two or more of such inorganic oxides. Examples of such mixtures are silica-chromium, silica-alumina, and silica-titania.

[0048] The inorganic oxide support material is porous and has variable surface area, pore volume, and average particle size. In some embodiments, the surface area is from 50 to 1000 square meter per gram (m^2/g) and the average particle size is from 20 to 300 micrometers (μm). Alternatively, the pore volume is from 0.5 to 6.0 cubic centimeters per gram (cm^3/g) and the surface area is from 200 to 600 m^2/g. Alternatively, the pore volume is from 1.1 to 1.8 cm^3/g and the surface area is from 245 to 375 m^2/g. Alternatively, the pore volume is from 2.4 to 3.7 cm^3/g and the surface area is from 410 to 620 m^2/g. Alternatively, the pore volume is from 0.9 to 1.4 cm^3/g and the surface area is from 390 to 590 m^2/g. Each of the above properties are measured using conventional techniques known in the art.

[0049] The support material may comprise silica, alternatively amorphous silica (not quartz), alternatively a high surface area amorphous silica (e.g., from 500 to 1000 m^2/g). Such silicas are commercially available from several sources including the Davison Chemical Division of W.R. Grace and Company (e.g., Davison 952 and Davison 955 products), and PQ Corporation (e.g., ES70 product). The silica may be in the form of spherical particles, which are obtained by a spray-drying process. Alternatively, MS3050 product is a silica from PQ Corporation that is not spray-dried. As procured, these silicas are not calcined (i.e., not dehydrated). Silica that is calcined prior to purchase may also be used as the support material.

[0050] Prior to being contacted with a catalyst, the support material may be pre-treated by heating the support material in air to give a calcined support material. The pre-treating comprises heating the support material at a peak temperature from 350° to 850° C., alternatively from 400° to 800°C., alternatively from 400° to 700°C., alternatively from 500° to 650°C. and for a time period from 2 to 24 hours, alternatively from 4 to 16 hours, alternatively from 8 to 12 hours, alternatively from 1 to 4 hours, thereby making a calcined support material. The support material may be a calcined support material.

[0051] The method may further employ a trim catalyst. The trim catalyst may be any one of the aforementioned metallocene catalysts made from the metal-ligand complex of formula (I) and activator. For convenience the trim catalyst is fed in solution in a hydrocarbon solvent (e.g., mineral oil or heptane). The hydrocarbon solvent may be the ICA. The trim catalyst may be made from the same metal-ligand complex of formula (I) as that used to make the metallocene catalyst of the bimodal catalyst system, alternatively the trim catalyst may be made from a different metal-ligand complex of formula (I) than that used to make the metallocene catalyst of the bimodal catalyst system. The trim catalyst may be used to vary, within limits, the amount of the metallocene catalyst used in the method relative to the amount of the single-site non-metallocene catalyst of the bimodal catalyst system. Each catalyst of the bimodal catalyst system is activated by contacting it with an activator. Any activator may be the same or different as another and independently may be a Lewis acid, a non-coordinating ionic activator, or an ionizing activator, or a Lewis base, an alkylaluminum, or an alkylaluminoxane (alkylalumoxane). The alkylaluminum may be a trialkylaluminum, alkylaluminum halide, or alkylaluminum alkoxide (diethylaluminum ethoxide). The trialkylaluminum may be trimethylaluminum, triethylaluminum ("TEAl"), tripropylaluminum, or tris(2-methylpropyl)aluminum. The alkylaluminum halide may be diethylaluminum chloride. The alkylaluminum alkoxide may be diethylaluminum ethoxide. The alkylaluminoxane may be a methylaluminoxane (MAO), ethylaluminoxane, 2-methylpropyl-aluminoxane, or a modified methylaluminoxane (MMAO). Each alkyl of the alkylaluminum or alkylaluminoxane independently may be a (C_1-C_7)alkyl, alternatively a (C_1-C_6)alkyl, alternatively a (C_1-C_4)alkyl. The molar ratio of activator's metal (Al) to a particular catalyst compound's metal (catalytic metal, e.g., Zr) may be 1000:1 to 0.5:1, alternatively 300:1 to 1:1, alternatively 150:1 to 1:1. Suitable activators are commercially available.

[0052] Once the activator and the catalysts of the bimodal catalyst system contact each other, the catalysts of the bimodal catalyst system are activated and activator species may be made *in situ*. The activator species may have a different structure or composition than the catalyst and activator from which it is derived and may be a by-product of the activation of the catalyst or may be a derivative of the by-product. The corresponding activator species may be a derivative of the Lewis acid, non-coordinating ionic activator, ionizing activator, Lewis base, alkylaluminum, or alkylaluminoxane, respectively. An example of the derivative of the by-product is a methylaluminoxane species that is formed by devolatilizing during spray-drying of a bimodal catalyst system made with methylaluminoxane.

[0053] Each contacting step between activator and catalyst independently may be done either in a separate vessel outside the GPP reactor (e.g., outside the FB-GPP reactor) or in a feed line to the GPP reactor. In option (a) the bimodal catalyst system, once its catalysts are activated, may be fed into the GPP reactor as a dry powder, alternatively as a slurry in a non-polar, aprotic (hydrocarbon) solvent. The activator(s) may be fed into the reactor in "wet mode" in the form of a solution thereof in an inert liquid such as mineral oil or toluene, in slurry mode as a suspension, or in dry mode as a powder. Each contacting step may be done at the same or different times.

[0054] TEST METHODS

[0055] Density

[0056] Density is measured in accordance with ASTM D792 and expressed in grams/cm^3 (g/cm^3 or g/cc).

[0057] Melt Flow Rate (I5 and I21)

[0058] The procedure described in ASTM D1238 is followed to determine the melt flow rate. Method B of ASTM D1238 is used. Samples are ran with loads of 21.6 kg or 5.0 kg (i.e., I21 or I5, respectively).

[0059] Absolute GPC (Molecular Weight Distribution)

[0060] The chromatographic system consists 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.

[0061] 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.

[0062] 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.

[0063] 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 nombiinal flowrate.

[0064] Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample)) (EQ1)

[0065] 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 > Mw/Mn > 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.

[0066] 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 viral coefficient effects (concentration effects on molecular weight).

[0067] 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 the following equations:

$$M_n(abs) = \frac{\sum^i IR_i}{\sum^i (IR_i / M_{absolute_i})}$$

$$M_w(Abs) = \frac{\sum^i IR_i \times M_{Absolute_i}}{\sum^i IR_i}$$

$$M_z(Abs) = \frac{\sum^i (IR_i \times M_{absolute_i}{}^2)}{\sum^i (IR_i \times M_{absolute_i})}$$

The absolute GPC chromatogram has a log M axis containing 601 equally-spaced Log(M) points, spaced by 0.01, between 2 and 8, which represents the molecular weight range between 100 and 100,000,000 where Log is the logarithm function to the base 10. Area fractions of the absolute molecular weight distribution plot were determined by integrating the plot to calculate the area between two defined limits, for example between LogM = 10^5 and LogM = 10^5.7, or between a defined limit and the plot curve reaching the axis at dWf/dLogM = 0, for example the area below LogM = 10^4 or the area above LogM = 10^5.4. Figure 1 visually demonstrates these defined are regions by different patterned vertical integration limits and different symbols to fill the area under the curve within the defined molecular weight ranges.

[0068] ESCR

[0069] To measure ESCR, the pellet samples were compression molded at 190° C. into a 0.075 inch sheet according to ASTM D4703 per Annex A.1 Procedure C. The compression molded sheet was conditioned at 23° C. (+/−2° C.) and 50% RH (+/−10% RH) for at least 24 hours before the individual coupons were stamped out using an appropriate die. The coupon dimensions were 38 mm×13 mm with a thickness of 1.90 mm. The coupons were further conditioned at 23° C. (+/−2° C.) and 50% RH (+/−10% RH) and tested at least 40 hours after compression molding and within 96 hours of compression molding. ESCR was measured according to ASTM-D 1693-01, Condition B. The sample thickness was measured to ensure they were within the ASTM 1693-01 specifications. Immediately prior to testing, the samples were notched to the required depth and then bent and loaded into the specimen holder. The holder was then placed in a test tube filled with a 10 percent, by volume, Tergitol NP-9 (Dow Chemical) aqueous solution, maintained at 50° C. The F50 failure time is reported.

[0070] 1% Secant Flexural Modulus

[0071] Flexural Testing were conducted according to ASTM D790. The polymer pellet samples are compression molded at 190°C to a nominal thickness of 0.125 inch according to ASTM D4703 per Appendix A.1 Procedure C. Samples are conditioned at 23 (± 2) °C and 50 (± 10) % R.H. for at least 40 hours. Sample geometry (length, depth, thickness) is 5" x 0.5" x 0.125". Samples are tested flatwise with a span of 2" for ASTM. Test speed is such that the flexural-strain rate on the outer surface is 1%/min, translating to 0.05 in/min. Additionally testing allows for a strain rate of 10%/min. From the resulting stress-strain data, Flexural modulus is reported from the initial slope of the curve. Secant modulus at 1% and 2% are reported as the slope of the line from the origin to a 1% and 2% strain, respectively.

[0072] Charpy Impact

[0073] Charpy testing is performed following ISO 179. Samples are fabricated from compression molded sheets. For compression molding, the pellet samples were molded at 190 °C to a nominal thickness of 4 mm. The pellets were weighed and placed in an appropriate picture frame chase. The chase has Mylar release sheets on each side and with copper or brass plates backing. The sample is placed in a hot press under low, contact pressure (3,000 psi) for 4 minutes and then placed under high pressure (30,000 psi) for a further 6 minutes. After this, the sample is controlled cooled at 15 °C/min (+/- 2 °C/min) until the sample is at approximately 35 °C at which point it is removed from the press. Specimens are cut from the sheet with an appropriate die to give samples 80 mm in length and 10 mm in width. The samples are notched on the long side in the thickness direction using an automated notcher to leave a ligament width of 8mm. The notching half angle is 22.5° and the radius of curvature at the tip is 0.25mm. The samples are conditioned for at least 40 hours at 23+/-2 °C and 50+/-10 % R.H. For samples that are tested at non-ambient temperatures, the specimens are further conditioned at the test temperature for a minimum of 1 hour. Specimens are loaded into the Charpy Izod tester with the notch directed away the impactor. The pendulum is released and the energy absorbed during the test is automatically recorded. The specimen is examined post-test and the type of failure noted (Complete, hinged, partial or no-break). Ten replicates are tested per sample per temperature.

[0074] Melt Strength

[0075] Melt strength is determined with a Göttfert Rheotens unit model 71.9 in combination with a capillary rheometer (such as Rheotester 2000 and Rheograph 25 from Göttfert, e.g.). A polymer melt (about 20-30 grams, pellets) is extruded through a capillary die with a flat entrance angle (180 degrees), diameter of 2.0 mm, and length of 30 mm. After equilibrating the samples at 190° C. for 10 minutes, molten polymer is extruded out of the die at a constant volume flow rate corresponding to a theoretical average exit velocity of 9.5 mm/s and an apparent wall shear rate of 38.2 s-1. The wheels of the Rheotens were at standard laboratory temperature. The distance between the die exit and the wheels was 100 mm. The extruded strand was drawn by a set of standard smooth wheels with a 0.4 mm gap. The wheels were accelerated at a rate of 2.4 mm/s2 and the tensile force recorded as a function of take-up speed until the filament broke. The velocity at break is a measure for the drawability of the polymer melt. Melt strength is defined as the plateau value of the force-velocity curve just before the strand broke and is reported in Centinewton (cN).

[0076] **EXAMPLES**

[0077] Materials Used

[0078] The following materials were included in the examples discussed below.

[0079] Comparative Example (CE) 3 and CE 4 are unimodal, gas phase resins.

[0080] Preparation of Comparative Examples 1, 2, 5 and Inventive Examples 1, 2, and 3

[0081] Bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl is the compound of formula (II) wherein M is Zr and each R is benzyl ("Bn"). It may be made by procedures described in the art or obtained from Univation Technologies, LLC, Houston, Texas, USA, a wholly-owned entity of The Dow Chemical Company, Midland, Michigan, USA. Representative Group 15-containing metal compounds, including bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl, and preparation thereof can be as discussed and described in U.S. Pat. Nos. 5,318,935; 5,889,128; 6,333,389; 6,271,325; 6,689,847; and 9,981,371; and WO Publications WO 99/01460; WO 98/46651; WO 2009/064404; WO 2009/064452; and WO 2009/064482.

[0082] CA-300: a continuity additive available from Univation Technologies, LLC. Added to gas phase polymerization reactor to decrease static buildup.

[0083] UT-TR-300: a catalyst additive available from Univation Technologies, LLC consisting of 1.0 Wt. % active organometallic compound. Added to gas phase polymerization to adjust product I21.

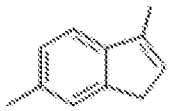
[0084] 1-hexene Comonomer: $H_2C=C(H)(CH_2)_3CH_3$. Comonomer co-polymerized with ethylene in the gas phase polymerization reactor.

[0085] Ethylene ("C_2"): $CH_2=CH_2$. Monomer polymerized in the gas phase polymerization reactor. When copolymerized with 1-hexene, makes ethylene/1-hexene copolymer.

[0086] ICA: a mixture consisting essentially of at least 95%, alternatively at least 98% of 2-methylbutane (isopentane) and minor constituents that at least include pentane ($CH_3(CH_2)_3CH_3$). May be added to the gas phase polymerization reactor to enable condensing mode operation thereof.

[0087] Molecular hydrogen gas: H_2. May be added to the gas phase polymerization reactor to alter molecular weight of the polyethylene produced therein.

[0088] Mineral oil: Sonneborn HYDROBRITE 380 PO White. May be used as a carrier liquid for feeding catalyst into a gas phase polymerization reactor.

[0089] Preparation 1: synthesis of 3,6-dimethyl-1*H*-indene, of the formula  . In a glove box, a 250-mL two-neck container fitted with a thermometer (side neck) and a solids addition funnel, was charged with tetrahydrofuran (25 mL) and methylmagnesium bromide (2 equivalents, 18.24 mL, 54.72 mmol). The contents of the container were cooled in a freezer set at -35 °C for 40 minutes; when removed from the freezer, the contents of the container were measured to be -12 °C. While stirring, indanone [5-Methyl-2,3-dihydro-1H-inden-1-one (catalog #HC-2282)] (1 equivalent, 4.000 g, 27.36 mmol) was added to the container as a solid in small portions and the temperature increased due to exothermic reaction; additions were controlled to keep the temperature at or below room temperature. Once the addition was complete, the funnel was removed, and the container was sealed (SUBA). The sealed container was moved to a fume hood (with the contents already at room temperature) and put under a nitrogen purge, then stirred for 3 hours. The nitrogen purge

was removed, diethyl ether (25 mL) was added to the container to replace evaporated solvent, and then the reaction was cooled using an acetone/ice bath. A HCl (15% volume) solution (9 equivalents, 50.67 mL, 246.3 mmol) was added to the contents of the container very slowly using an addition funnel, the temperature was maintained below 10 °C. Then, the contents of the container were warmed up slowly for approximately 12 hours (with the bath in place). Then, the contents of the container were transferred to a separatory funnel and the phases were isolated. The aqueous phase was washed with diethyl ether (3 times 25 mL). The combined organic phases were then washed with sodium bicarbonate (50 mL, saturated aqueous solution), water (50 mL), and brine (50 mL). The organic phase was dried over magnesium sulfate, filtered and the solvent removed by rotary evaporator. The resulting dark oil, confirmed as product by NMR, was dissolved in pentane (25 mL), then filtered through a short silica plug (pre-wetted with pentane) that was capped with sodium sulfate. Additional pentane (25-35 mL) was used to flush the plug, then were combined with the first. The solution was dried by rotary evaporator resulting in 2.87 g (74% yield) of 3,6-dimethyl-1H-indene that was confirmed as product by NMR. ^{1}H NMR (C_6D_6): 7.18 (d, 1H), 7.09 (s, 1H), 7.08 (d, 1H), 5.93 (m, 1H), 3.07 (m, 2H), 2.27 (s, 3H), 2.01 (q, 3H).

[0090] Preparation 2: synthesis of (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl, which is a compound of formula (I) wherein R is H and each X is methyl. In a glovebox under an anhydrous inert gas atmosphere (anhydrous nitrogen or argon gas), 3,6-dimethyl-1H-indene (1.000g, 6.94 moles) in dimethoxyethane (10 mL) was added to a 120 mL (4-ounce (oz)) container, which was then capped, and the contents of the container were chilled to -35 °C. *n*-butyllithium (1.6M hexanes, 4.3 mL, 0.0069 mole) was added to the container and the contents were stirred for approximately 3 hours while heat was removed to maintain the contents of the container near -35 °C. Reaction progress was monitored by dissolving a small aliquot in d8-THF for ^{1}H NMR analysis; when the reaction was complete, solid cyclopentadienyl zirconium trichloride ($CpZrCl_3$) (1.821 g) was added in portions to the contents of the container while stirring. Reaction progress was monitored by dissolving a small aliquot in d8-THF for ^{1}H NMR analysis; the reaction was complete after approximately 3 hours and the contents of the container were stirred for approximately 12 more hours. Then, methylmagnesium bromide (3.0M in ether, 4.6 mL) was added to the contents of the container, after the addition the contents of the container were stirred for approximately 12 hours. Then, solvent was removed in vacuo and the product was extracted into hexane (40 mL) and filtered

through diatomaceous earth, washed with additional hexane (30 mL) and then dried in vacuo to provide the cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl. (Cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) analysis. ^{1}H NMR (C_6D_6): □□ 7.26 (d, 1H), 6.92 (d, 1H), 6.83 (dd, 1H), 5.69 (d, 1H), 5.65 (m, 1H), 5.64 (s, 5H), 2.18 (s, 3H), 2.16 (s, 3H), -0.34 (s, 3H), -0.62 (s, 3H).

[0091] Due to the rules of IUPAC nomenclature it is believed that the dimethyl numbering in the molecule 3,6-dimethyl-1*H*-indene becomes, after deprotonation thereof, becomes in the conjugate anion 1,5-dimethylindenyl.

[0092] Preparation 3: Preparation of Bimodal Catalyst System 1 (AFS-BMCS1). Slurry 70.3 parts by weight of treated fumed silica (CABOSIL TS-610) in 1000 parts by weight of toluene, followed by adding 171 parts by weight of a 30 wt% solution of methylaluminoxane (MAO) in toluene, 3.54 parts by weight of the bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl and 0.229 parts by weight of cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl of Preparation 2 to give a mixture. Using a spray dryer set at 160° C. and with an outlet temperature at 70° to 80° C., introduce the mixture into an atomizing device of the spray dryer to produce droplets of the mixture, which are then contacted with a hot nitrogen gas stream to evaporate the liquid from the mixture to give a powder. Separate the powder from the gas mixture in a cyclone separator and discharge the separated powder into a container to give the Bimodal Catalyst System 1 ("BMCS1") as a fine powder. Slurry the resultant powder form of BMCS1 to give an activator formulation slurry form of BMCS1 ("AFS-BMCS1") of 22 wt% solids in 10 wt% isoparaffin fluid and 68 wt% mineral oil.

[0093] Preparation 4: preparation of Trim Catalyst Solution 1 ("TCS1") comprising a trim solution of cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl in n-hexane and isopentane. Charge (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl of Preparation 2 and n-hexane into a first cylinder. Charge the resulting solution of (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl solution in hexane from the first cylinder into a 106 liter (L; 28 gallons) second cylinder. The second cylinder contained 310 grams of 1.07 wt % (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl. Added 7.98 kg (17.6 pounds) of high purity isopentane to the 106 L cylinder to yield the Trim Catalyst Solution 1 of 0.04 wt % (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl in n-hexane and isopentane.

[0094] Preparation 5. preparation of Trim Catalyst Solution 2 ("TCS2"). Charge UT-TR-300 into a first cylinder. Charge the resulting solution of UT-TR-300 from the first cylinder into a 106 liter (L; 28 gallons) second cylinder. The second cylinder contained 1452.8 grams of UT-TR-300. Added 34.9 kg (76.8 pounds) of high purity isopentane to the 106 L cylinder to yield the Trim Catalyst Solution 2.

[0095] Polymerization Procedure. For Inventive Example 1-5 described below, copolymerized ethylene and 1-hexene using the Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and a controlled relative amount of the Trim Catalyst Solution 1 (TCS1) or Trim Catalyst Solution 2 (TCS2) in a fluidized bed-gas phase polymerization (FB-GPP) reactor having a distribution grid to make an embodiment of the bimodal poly(ethylene-*co*-1-alkene) copolymer that is a bimodal poly(ethylene-*co*-1-hexene) copolymer. The FB-GPP reactor had a 0.35 meter (m) internal diameter and 2.3 m bed height and a fluidized bed composed of polymer granules. Flowed fluidization gas through a recycle gas loop comprising sequentially a recycle gas compressor and a shell-and-tube heat exchanger having a water side and a gas side. The fluidization gas flows through the compressor, then the water side of the shell-and-tube heat exchanger, then into the FB-GPP reactor below the distribution grid. Fluidization gas velocity in the be is about 0.55 to 0.61 meter per second (m/s, 1.8 to 2.0 feet per second). The fluidization gas then exits the FB-GPP reactor through a nozzle in the top of the reactor, and is recirculated continuously through the recycle gas loop. Maintained a constant fluidized bed temperature by continuously adjusting the temperature of the water on the shell side of the shell-and-tube heat exchanger. Introduced feed streams of ethylene, nitrogen, and hydrogen together with the 1-hexene comonomer into the recycle gas line. Operated the FB-GPP reactor at a total pressure of about 2420 kPa gauge, and vented reactor gases to a flare to control the total pressure. Adjusted individual flow rates of ethylene, nitrogen, hydrogen and the 1-hexene to maintain their respective gas composition targets. Set ethylene partial pressure to 1.52 megapascal (MPa, 220 pounds per square inch (psi)), and set the C_6/C_2 molar ratio and the H_2/C_2 molar ratio as specified. Average copolymer residence time was 2.4 to 3.0 hours. Measured concentrations of all gasses using an on-line gas chromatograph. Maintained the fluidized bed at constant height by withdrawing a portion of the bed at a rate equal to the rate of formation of particulate product bimodal poly(ethylene-*co*-1-hexene) copolymer. Product was removed semi-continuously via a series of valves into a fixed volume chamber. A nitrogen purge removed a significant portion of entrained and dissolved hydrocarbons in the fixed volume chamber. After purging, the product was

discharged from the fixed volume chamber into a fiber pack for collection. The product was further treated with a small stream of humidified nitrogen to deactivate any trace quantities of residual catalyst and cocatalyst. Set the ratio feed of trim catalyst solution 1 (TCS1) or trim catalyst solution 2 (TCS2) to the feed of the bimodal catalyst system AFS-BMCS1 to adjust the HLMI (I_{21}) of the produced bimodal poly(ethylene-*co*-1-hexene) copolymer in the reactor to achieve the desired target. Set the catalyst feeds at rates sufficient to maintain a production rate of about 14 to about 18 kg/hour (about 31 to about 40 lbs/hr) of the bimodal poly(ethylene-*co*-1-hexene) copolymer.

[0096] Inventive Example 1 (IE1): synthesized an embodiment of the inventive bimodal poly(ethylene-*co*-1-hexene) copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer is 1-hexene, and Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and Trim Catalyst Solution 2 (TCS2).

[0097] Inventive Examples 2, 3 (IE2, and IE3) and Comparative Example 1 (CE1): synthesized an embodiment of the inventive bimodal poly(ethylene-*co*-1-hexene) copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer is 1-hexene, and Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and Trim Catalyst Solution 1 (TCS1).

[0098] Comparative Example 4 (CE4) is the same example as Inventive Example 15 of US20220169762A1, which is hereby incorporated in its entirety by reference. Comparative Example 2, 3 (CE2 and CE3) are unimodal resins made from chromium catalyst.

[0099] The polymerization conditions and process results are described in Table 1 below and the resin properties are described in Table 2 below.

[0100] **Table 1: Polymerization Conditions of IE1-3 and CE 1.**

Polymerization Conditions	**IE2**	**IE3**	**CE1**	**IE1**
Bed Temperature (° C.)	80	80	105	95
Reactor Pressure (kPa)	2420	2420	2420	2420
Ethylene ("C_2") Partial Pressure (kPa)	1517	1517	1517	1517
H_2/C_2 Molar Ratio	0.0006	0.0005	0.0002	0.0007

1-hexene/ethylene ("C_6/C_2") Molar Ratio	0.0007	0.0006	0.0002	0.0007
Induced Condensing Agent 1-methylbutane (mol%)	12.9	13.0	13.9	12.9
Superficial Gas Velocity (m/sec)	0.56	0.54	0.52	0.55
Bimodal Catalyst System	AFS-BMCS1	AFS-BMCS1	AFS-BMCS1	AFS-BMCS1
Trim Catalyst Solution	TCS1	TCS1	TCS1	TCS2
TCS/AFS-BMCS1 mass flow ratio	14.3	16.0	26.4	9.9
CA-300 Continuity Additive (ppm)	50	52	71	60
Catalyst Zr conc. (wt%)	0.45	0.45	0.45	0.45
Catalyst Al conc. (wt%)	19.80	19.80	19.80	19.80
Starting seedbed = granular HDPE resin	Preloaded	Preloaded	Preloaded	Preloaded
Fluidized Bed Weight (kg)	44	44	42	45
Copolymer Production Rate (kg/hour)	18	17	18	15
Copolymer Residence Time (hour)	2.4	2.5	2.4	3.0
Copolymer Fluid Bulk Density, (kg/m^3)	274	276	263	276

[0101] As shown in Table 1, the polymerization catalyst AFS-BMCS1 and TCS1 or TCS2 have been used under controlled gas phase polymerization process conditions to make a bimodal poly(ethylene-*co*-1-hexene) copolymer having the improved properties shown below in Table 2. Varying the TCS1/AFS-BMCS1 or TCS2/AFS-BMCS1 molar ratio can be used to

change the copolymer's I_{21} property. Varying the H_2/C_2 Molar Ratio and reactor temperature can be used to change the copolymer's molecular weight.

[0102] Formula (I), noted above is as follows: $(R^1{}_xCp)((alkyl)_yIndenyl)MX_2$ (I), wherein subscript x is 0 or 1; each R^1 independently is methyl or ethyl; subscript y is 1, 2, or 3; each alkyl independently is a $(C_1\text{-}C_4)$alkyl; M is titanium, zirconium, or hafnium; and each X is independently a halide, a $(C_1$ to $C_{20})$alkyl, a $(C_7$ to $C_{20})$aralkyl, a $(C_1$ to $C_6)$alkyl-substituted $(C_6$ to $C_{12})$aryl, or a $(C_1$ to $C_6)$alkyl-substituted benzyl.

[0103] Polyethylene compositional properties are measured in accordance with the test methods described above.

[0104] Table 2A – Properties of Inventive Examples 1-3

	IE1	IE2	IE3
Density	0.9546	0.9552	0.9550
I21	5.67	5.93	6.37
I5	0.13	0.12	0.17
I21/I5	43.6	50.7	38.1
1% Secant Flexrual Modulus (ksi, 0.5in/min)	176.6	173.4	173.6
ESCR (10% Igepal) F50	692	1000	639.7
Charpy Impact (-40 C, kJ/m2)	69.0	46.8	42
Melt Strength (cN)	20.0	20.0	18.0
ABS M_n	31,673	34,724	36,319
ABS M_w	323,673	501,613	340,422
ABS M_z	1,436,692	2,721,839	1,602,480

[0105] Table 2B – Properties of CE1-CE4

	CE1	CE2	CE3	CE4
Density	0.9517	0.9540	0.9460	0.954
I21	5.25	5.75	6.50	4.7
I5	0.61	0.16	0.17	0.16
I21/I5	8.6	35.9	38.2	30
1% Secant Flexural Modulus (ksi, 0.5in/min)	162.1	170.0	138.5	*NM
ESCR (10% Igepal) F50	93	213	1000	292

Charpy Impact (-40 C, kJ/m2)	78.0	29.0	10.3	58.3
Melt Strength (cN)	11.0	30.0	35.0	20.0
ABS M_n	62,183	11,523	8,476	32,877
ABS M_w	217,823	243,019	301,051	370,425
ABS M_z	957,176	1,322,367	2,562,108	2,549,541

[0106] Table 3 – GPC Fraction Properties of Examples

		IE1	IE2	IE3	CE1	CE2	CE3	CE4
abs Mw < 10^4 Da	<10%	7.35%	6.35%	5.61%	2.02%	13.78%	18.90%	7.27%
abs Mw 10^5.0-5.7 Da	*20~40%*	24.70%	20.75%	24.03%	47.09%	30.14%	26.26%	22.69%
abs Mw>10^5.4 Da	>25.5%	27.33%	29.10%	26.05%	18.89%	22.58%	21.87%	24.93%

[0107] As can be seen from the above tables, the inventive examples display a desirable balance of properties including melt strength, impact resistance, and ESCR. The Mw fraction (abs Mw < 10^4 Da) can be shown to negatively impact the Charpy impact strength given comparable density and mass flow rates. The Mw fraction (abs Mw > $10^{5.4}$ Da) can be shown to enhance the ESCR performance given comparable density and mass flow rates. The Mw fraction ($10^{5.7}$ Da > abs Mw > $10^{5.0}$ Da) can be shown to enhance the melt strength given comparable density and mass flow rates.

We Claim:

1. A multimodal polyethylene composition having a density of from 0.935 g/cm^3 to 0.980 g/cm^3, wherein the multimodal polyethylene composition has a molecular weight distribution as shown in a chromatogram characterized by absolute GPC as follows:

a) a first absolute GPC fraction of less than 10,000 Daltons less than 10.0%;

b) a second absolute GPC fraction of from $10^{5.0}$ to $10^{5.7}$ Daltons between 20.0 to 40.0%; and

c) a third absolute GPC fraction of greater than $10^{5.4}$ Daltons greater than 25.5%;

wherein percent (%) is based on percent area under the curve shown in the chromatogram characterized by absolute GPC.

2. The multimodal polyethylene composition of claim 1, wherein the multimodal polyethylene composition has a density from 0.950 to 0.960 g/cm^3.

3. The multimodal polyethylene composition of any preceding claim, wherein the composition has a high flow melt index (I_{21}) of from 4.0 to 7.0 g/10 min.

4. The multimodal polyethylene composition of any preceding claim, wherein the composition has an I_5 value of from 0.10 to 0.50 g/10 min.

5. The multimodal polyethylene composition of any preceding claim, wherein the composition has an I_{21}/I_5 in the range of from 30 to 60.

6. The multimodal polyethylene composition of any preceding claim, wherein the composition has at least one of the following: an environmental stress cracking resistance (ESCR) greater than 500 hours; a Charpy Impact value of greater than 40 kJ/m^2; a melt strength of greater than 15.0 centinewtons (cN); or a 1% secant flexural modulus (0.5 in/min) of greater than 155 ksi.

7. A blow molding process comprising the steps of: (1) placing a quantity of molten polyethylene in a mold cavity, (2) blowing a gas into the molten polyethylene, causing it to expand and assume the approximate shape of the mold cavity, and (3) cooling the molten polyethylene, wherein the molten polyethylene is the multimodal polyethylene composition of any one of claims 1 to 6.

8. A blow molded article prepared by the process of claim 7.

9. A blow molded article comprising the multimodal polyethylene composition of any one of claims 1 to 6.

10. The multimodal polyethylene composition of any one of claims 1 to 6, wherein the multimodal polyethylene compositions is made by the process of polymerizing ethylene and an alpha-olefin comonomer in the presence of a bimodal catalyst system in a single gas phase polymerization (GPP).

FIGURE 1

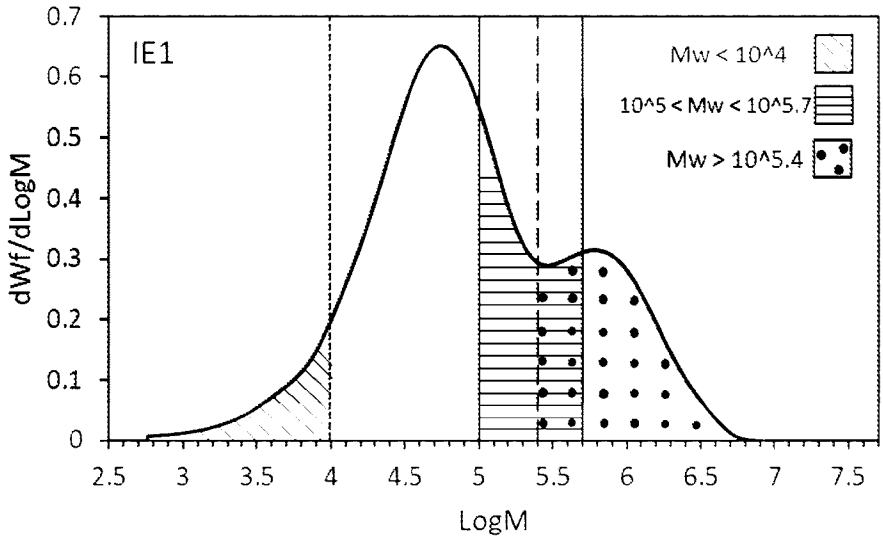


FIGURE 2

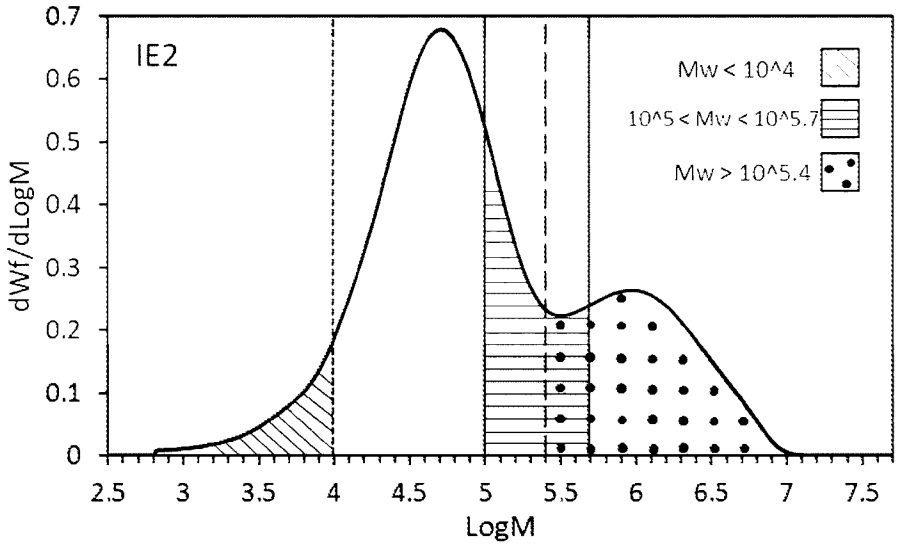
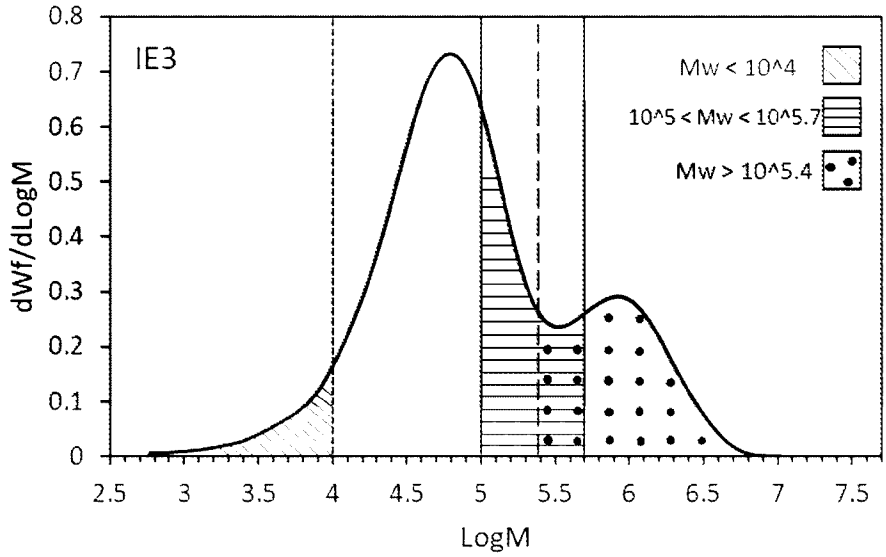


FIGURE 3


IE3
Mw < 10^4
10^5 < Mw < 10^5.7
Mw > 10^5.4
dWf/dLogM
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
LogM

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/046391

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/08 C08F210/16 C08F4/659
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/169762 A1 (ASKAR SHADID [US] ET AL) 2 June 2022 (2022-06-02) IE14 and IE15 IE10-IE12 paragraph [0105] paragraph [0099] paragraph [0107] paragraph [0007] paragraph [0020] -----	1-10
X	WO 2015/138673 A1 (CHEVRON PHILLIPS CHEMICAL CO [US]) 17 September 2015 (2015-09-17) examples 2,3 page 60, line 20 - page 61, line 18 tables 2,4 ----- -/--	1-10

[x] Further documents are listed in the continuation of Box C. [x] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2024	28/11/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Thomas, Dominik

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/046391

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2023/069407 A1 (UNIVATION TECH LLC [US]) 27 April 2023 (2023-04-27) examples - - - - -	1-10

4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/046391

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2022169762 A1	02-06-2022	BR 112021019432 A2	30-11-2021
		CA 3137110 A1	05-11-2020
		CN 113728020 A	30-11-2021
		EP 3962972 A1	09-03-2022
		SG 11202110973P A	29-11-2021
		US 2022169762 A1	02-06-2022
		WO 2020223191 A1	05-11-2020
WO 2015138673 A1	17-09-2015	CN 104910305 A	16-09-2015
		EP 3116923 A1	18-01-2017
		ES 2808108 T3	25-02-2021
		US 2015259455 A1	17-09-2015
		US 2016122454 A1	05-05-2016
		US 2017096512 A1	06-04-2017
		WO 2015138673 A1	17-09-2015
WO 2023069407 A1	27-04-2023	CA 3235407 A1	27-04-2023
		CN 118139902 A	04-06-2024
		EP 4419571 A1	28-08-2024
		KR 20240089656 A	20-06-2024
		US 2024376236 A1	14-11-2024
		WO 2023069407 A1	27-04-2023