

PROCESSES FOR MAKING MULTIMODAL ETHYLENE-BASED POLYMERS**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/510,766 filed June 28, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments are generally related to processes for producing ethylene-based polymer and are particularly related to processes for producing ethylene-based polymers, which provide processibility and dart strength in films.

BACKGROUND

[0003] Linear Low Density Polyethylenes (LLDPE) made via solution or gas phase processes typically have excellent mechanical properties, but poor melt strength and processibility in film fabrication. Therefore, to increase processibility, some amount of LDPE may typically be blended with LLDPE in order to improve the processibility and melt strength of LLDPE resins. Unfortunately, the addition of LDPE leads to decreased mechanical properties of the resulting blends when compared with pure LLDPE resin.

[0004] Accordingly, there are needs for ethylene-based polymers suitable to provide processibility and excellent mechanical properties (e.g., dart) without blending with LDPE.

SUMMARY

[0005] The present ethylene-based polymers achieve this need for processibility and mechanical strength by including at least one polymer fraction having increased long chain branching. Without being limited by theory, this long chain branching provides increased melt strength necessary in film processing, while the ethylene-based polymers still maintain excellent abuse resistance properties in films.

[0006] According to one or more embodiments, embodiments are directed to a process for producing ethylene-based polymer in a reactor system comprising a first reactor and a second reactor. The process comprises polymerizing ethylene, one or more (C₃-C₁₄) α -olefin monomers,

and at least one polyene, in the presence of one multi-chain catalyst and at least one single-chain catalyst in the first reactor to produce a first reactor polyethylene product comprising long chain branching, wherein the multi-chain catalyst comprises a plurality of polymerization sites, and wherein the long-chain branching occurs by connecting two polymer chains of the multi-chain catalyst with the polyene in a concerted fashion during the polymerization; and polymerizing ethylene and one or more (C₃-C₁₄) α -olefin monomers in the absence of an initial polyene feed and in the presence of at least one single-chain catalyst in the second reactor to produce a second reactor polyethylene product, wherein the ethylene-based polymer comprises the first and second reactor polyethylene products.

[0007] These and embodiments are described in more detail in the following Detailed Description in conjunction with the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] 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:

[0009] FIG. 1 graphically depicts the molecular weight distribution of the present ethylene-based polymers according to one or more embodiments presently described; and

[0010] FIG. 2 graphically illustrates the relationship between melt strength and normalized dart strength for the present ethylene-based polymers according to one or more embodiments presently described.

DETAILED DESCRIPTION

[0011] Specific embodiments of a process for synthesizing polymer and polymers synthesized by the process of this disclosure will now be described. It should be understood that the process for synthesizing polymers 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.

[0012] DEFINITIONS

[0013] The term “polymer” refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term “homopolymer,” usually employed to refer to polymers prepared from only one type of monomer as well as “copolymer” which refers to polymers prepared from two or more different monomers.

[0014] “Polyethylene” or “ethylene-based polymer” shall mean polymers comprising greater than 50% by weight of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of polyethylene known in the art include 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).

[0015] 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 0.930 g/cm³.

[0016] 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. 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.

[0017] “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.

[0018] “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).

[0019] As used herein, “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.

[0020] As used herein, the term “polyene” refers to comonomers having at least two double bonds. Polyenes encompass “dienes”, which are comonomers with two double bonds.

[0021] The term “gel” or “gelling” refers to a solid composed of at least two components: the first is a three dimensional cross-linked polymer and the second is a medium in which the polymer

does not fully dissolve. When the polymer gels and does not fully dissolve, the reactor may become fouled with polymer gel.

[0022] The term “long-chain branching” refers to branches having greater than 100 carbon atoms. A “branch” refers to a portion of polymer that extends from a tertiary or quaternary carbon atom. When the branch extends from a tertiary carbon atom, there are two other branches, which collectively could be the polymer strand from which the branch extends. Polymer strands are linear segments of a polymer, or more specifically a copolymer, which are optionally joined at the end(s) by branching junctures. For example, a tetra-functional branch juncture joins the ends of four polymer strands, as opposed to a tri-functional branch juncture, which joins the ends of three polymer strands.

[0023] 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.

[0024] *Ethylene-based Polymers*

[0025] Embodiments of the present disclosure are directed to ethylene-based polymers, in specific embodiments, trimodal ethylene-based polymers comprising first, second, and third polymer fractions. The first, second, and third polymer fractions each comprise the polymerized reaction product of ethylene monomer and optionally C₃-C₁₄ alpha-olefin comonomer with the proviso that at least one of the first, second, and third polymer fractions comprise the polymerized reaction product of ethylene monomer, polyene comonomer, and optionally C₃-C₁₄ alpha-olefin comonomer.

[0026] In one or more embodiments, the polyenes may comprise acyclic unconjugated dienes. The acyclic unconjugated dienes may comprise one or more of 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-

dodecadiene, dimethyldivinylsilane, dimethyldiallylsilane, dimethylallylvinylsilane. The polyene may not include cyclic or bicyclic polyenes, for example, norbornene based compounds, because these cyclic or bicyclic polyenes do not incorporate effectively into polymer chains to produce long chain branching.

[0027] The C₃-C₁₄ alpha-olefin comonomer may include one or more of 1-propylene, 1-butene, 1-hexene, 1-octene, or combinations thereof.

[0028] As noted above, the present trimodal ethylene-based polymer has excellent processibility, which can be quantified in part by its melt strength. As further noted above, this processibility and melt strength is attributed to the long chain branching present in the trimodal-ethylene-based polymer. In one or more embodiments, the trimodal ethylene-based polymer may have a melt strength (MS) from 4.0 to 25.0 cN wherein 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 further embodiments, the melt strength (MS) is from 4.0 to 20.0 cN, 4.0 to 15.0 cN, 8.0 to 15.0 cN, or 9.0 to 14.0 cN.

[0029] Moreover, the trimodal ethylene-based polymer may have a rheology ratio $V_{0.1}/V_{100}$ from 4.0 to 12.0, wherein $V_{0.1}$ is the viscosity of the trimodal ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100} is the viscosity of the trimodal ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second. In further embodiments, the rheology ratio $V_{0.1}/V_{100}$ is from 4.0 to 8.0, or from 4.0 to 6.5. Without being limited by theory, rheology ratios are indicative of shear thinning, and increased long chain branching correlates to increased shear thinning. However, in the present case, shear thinning may be controlled in the trimodal ethylene-based polymer, for example, by producing one or multiple fractions in the trimodal ethylene-based polymer in addition to small amounts of long chain branching.

[0030] The trimodal ethylene-based polymer may have a melt index (I_2) of 0.5 to 2.0 dg/min, or from 0.5 to 1.0 dg/min wherein I_2 is measured according to ASTM D1238 (2.16 Kg/190 °C). The trimodal ethylene-based polymer may have an I_{10}/I_2 ratio of 5 to 15, or from 5 to 10.

[0031] In one or more embodiments, the trimodal ethylene-based polymer has a density of 0.910 to 0.935 g/cc, from 0.910 to 0.920 g/cc, or from 0.912 to 0.920 g/cc.

[0032] In one or more embodiments, the trimodal ethylene-based polymer has a molecular weight distribution (MWD) of 3 to 5, wherein MWD is defined as M_w/M_n with M_w being a weight average molecular weight and M_n being a number average molecular weight as measured according to conventional Gel Permeation Chromatography. Furthermore, the trimodal ethylene-based polymer has an M_n of 20.0 to 35.0 kg/mol, or from 25.0 to 35.0 kg/mol. Furthermore, the trimodal ethylene-based polymer has an M_w of 100.0 to 130.0 kg/mol, or from 105.0 to 125.0 kg/mol.

[0033] *Process*

[0034] Various processes and processing parameters are considered suitable for producing the multimodal and trimodal ethylene-based polymers of the present disclosure. In one or more embodiments, a process for producing multimodal ethylene-based polymers (e.g., the trimodal ethylene-based polymer) in a reactor system comprises a first reactor and a second reactor. The process comprises polymerizing the ethylene, one or more (C_3 - C_{14}) α -olefin monomers, and at least one polyene, in the presence of one multi-chain catalyst and at least one single-chain catalyst in the first reactor to produce a first reactor polyethylene product comprising long chain branching. The multi-chain catalyst comprises a plurality of polymerization sites, and wherein the long-chain branching occurs by connecting two polymer chains of the multi-chain catalyst with the polyene in a concerted fashion during the polymerization. In the second reactor, ethylene and one or more (C_3 - C_{14}) α -olefin monomers are polymerized in the absence of an initial polyene feed and in the presence of at least one single-chain catalyst to produce a second reactor polyethylene product. The trimodal ethylene-based polymer comprises the first and second reactor polyethylene products.

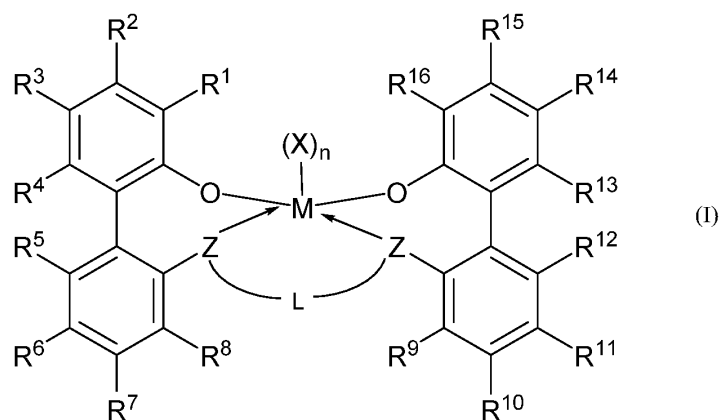
[0035] It is contemplated that the polymerization reactions may involve solution polymerization, slurry polymerization, or gas phase polymerization. In specific embodiments, solution polymerization is conducted in the first reactor, the second reactor, or both. The first reactor and second reactor, may be in parallel or in series. 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.

[0036] Exemplary solvents used in the solution polymerization process may include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR™ E from ExxonMobil Chemical.

[0037] As stated above, one or more single-chain catalysts may be in the first reactor, and the second reactor. In one embodiment, the first reactor and the single-chain catalyst may both comprise one single-chain catalyst.

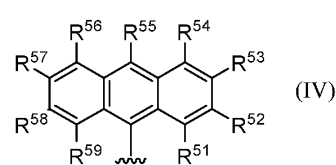
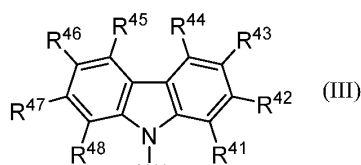
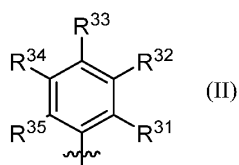
[0038] As used herein, “single-chain catalyst”, which may also be called a single-site catalyst, is a polymerization catalyst having one active polymerization site and/or reactive metal center. Various single-chain catalysts are considered suitable. These may include bis-metallocene catalysts, phosphinimine, constrained geometry catalysts, post-metallocene catalysts and single site molecular catalysts, including, but not limited to, bis(biphenylphenoxy) catalysts (also referred to as polyvalent aryloxyether catalysts).

[0039] In one embodiment, the single-chain catalyst in the first reactor, the second reactor, or both comprises a bis(biphenylphenoxy) catalyst. According to some embodiments, the bis(biphenylphenoxy) catalyst has a structure according to formula (I):



[0040] 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. Subscript n of (X)_n is 0, 1, or 2. When subscript n is 1, X is a monodentate ligand or a bidentate ligand, and when subscript n is 2, each X is chosen from a monodentate ligand. Each Z is independently chosen from -O-, -S-, -N(R^N)-, or -P(R^P)-; R¹ and R¹⁶ are independently selected from the group consisting of -H, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C,

$-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):

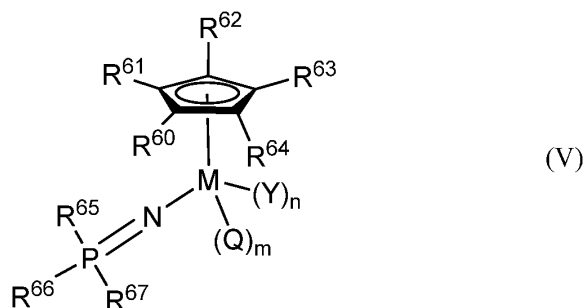


[0041] In formulas (II), (III), and (IV), each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-\text{H}$, $(\text{C}_1\text{-C}_{40})$ hydrocarbyl, $(\text{C}_1\text{-C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen, provided at least one of R^1 or R^{16} is a radical having formula (II), a radical having formula (III), or a radical having formula (IV).

[0042] In one or more embodiments, each X can be a monodentate ligand that, independently from any other ligands X, is a halogen, unsubstituted $(\text{C}_1\text{-C}_{20})$ hydrocarbyl, unsubstituted $(\text{C}_1\text{-C}_{20})$ hydrocarbyl $\text{C}(\text{O})\text{O}-$, or $\text{R}^{\text{K}}\text{R}^{\text{L}}\text{N}-$, wherein each of R^{K} and R^{L} independently is an unsubstituted $(\text{C}_1\text{-C}_{20})$ hydrocarbyl.

[0043] Additional details and examples of bis(biphenylphenoxy) catalysts are provided in PCT Publications WO2011/146291, WO2018/183056, WO2019/190925 and U.S. Patent 7060848B2, which are incorporated by reference herein in its entirety.

[0044] In one embodiment, the single-chain catalyst in the first reactor, the second reactor, or both may comprise a phosphinimine catalyst. The phosphinimine precatalysts may have a structure of formula (V):

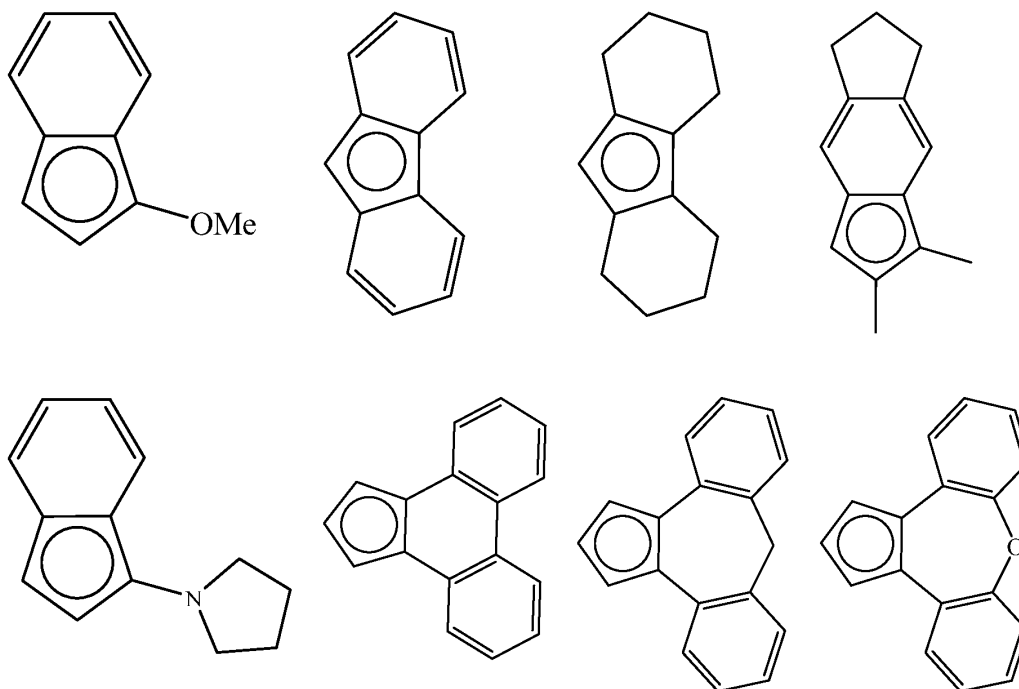


[0045] In formula (V), each Q is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, –CH₂Si(R^C)_{3-Q}(OR^C)_Q, –Si(R^C)_{3-J}(OR^C)_J, –OSi(R^C)_{3-J}(OR^C)_J, –CH₂Ge(R^C)_{3-J}(OR^C)_J, –Ge(R^C)_{3-J}(OR^C)_J, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –N(R^C)₂, –NH(R^C), –N(Si(R^C)₃)₂, –NR^CSi(R^C)₃, –NHSi(R^C)₃, –OR^C, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, –S(O)R^C, –S(O)₂R^C, –OS(O)₂R^C, –N=C(R^C)₂, –N=CH(R^C), –N=CH₂, –N=P(R^C)₃, –OC(O)R^C, –C(O)OR^C, –N(R^C)C(O)R^C, –N(R^C)C(O)H, –NHC(O)R^C, –C(O)N(R^C)₂, –C(O)NHR^C, –C(O)NH₂, a halogen, B(R^Y)₄, Al(R^Y)₄, or Ga(R^Y)₄, or a hydrogen, wherein each R^C is independently a (C₁–C₃₀)hydrocarbyl, or (C₁–C₃₀)heterohydrocarbyl, and each J is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is –H, (C₁–C₃₀)hydrocarbyl, or halogen atom, wherein two X ligands can be connected to form a metallacycle ring

[0046] In formula (V), each Y is independently Lewis Base; optionally, Q and Y can be linked to form a ring. Each subscript m is 1 and 2; and each subscript n is 0, 1 and 2. The metal–ligand complex is overall charge-neutral.

[0047] In formula (V), M₂ is titanium, zirconium, or hafnium; R⁶⁰, R⁶¹, R⁶², R⁶³, and R⁶⁴ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl wherein any of the R⁶¹, R⁶², R⁶³, and R⁶⁴ optionally are connected to form a ring structure; R⁶⁵, R⁶⁶, and R⁶⁷ are independently (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₆–C₃₀)aryl, (C₅–C₃₀)heteroaryl wherein two of R⁶⁵, R⁶⁶, and R⁶⁷ are optionally connected to form a ring.

[0048] In various embodiments, in formula (V), (A) R⁶⁰ and R⁶¹ are connected and form a ring and are optionally substituted by one or more R^S; or (B) R⁵² and R⁶³ are connected and form a ring and are optionally substituted by one or more R^S; or (C) both (A) and (B). Thus, when (A), (B), or (C) occur, the cyclopentadienyl of formula (V) have a structure selected from the group consisting of:



[0049] As stated above, the multi-chain catalyst produces a polymer fraction having long chain branching. The multi-chain catalyst is a metal-ligand catalyst having at least two polymerization sites, which facilitates the propagation of at least two separate polymer chains. Suitable multi-chain catalysts and their mechanism of action are described in PCT Publications WO2020/069364, WO2020/205585, and WO2021195502A1, which are incorporated by reference herein in their entirety and briefly summarized here. At a high level, long chain branched fractions are produced through the addition of polyenes, specifically acyclic unconjugated dienes, in the presence of the multi-chain catalyst. Polyenes add to the polymer chain in a similar manner to α -olefins, but leave a pendant vinyl group which can insert into a polymer chain a second time to create the long chain branches. As stated above, the multi-chain catalyst has at least two polymer chain sites that propagates two separate polymer chains. One alkene of the polyene is incorporated into one polymer chain, and it is believed that due to the close proximity of the propagation sites, the second alkene of the polyene is then quickly incorporated into the second polymer chain, thereby forming a bridge or rung. This successive addition of diene is referred to as a “concerted” addition of the polyene, distinguishing it from catalysts without two proximal

chains where polyene addition leads to a concentration of vinyl containing polymers in the reactor, which react at a later time. The concerted addition of a polyene has been referred to as the “Ladder” mechanism. The term “rung” refers to the diene once it is incorporated into two separate polymer strands, thereby linking the strands together. The first and second polymer strands may continue to propagate until the polymer is released from the catalyst, the catalyst dies, or another diene is added.

[0050] Embodiments of the present disclosure utilize a multi-chain catalyst and a single-chain catalyst in the first reactor minimally. Without being bound by theory, the single-chain catalyst will polymerize ethylene and optionally alpha-olefin comonomer, but does not create appreciable amounts of long chain branching with the polyene, specifically because the single-chain catalyst does not produce two polymer chains in close proximity in which the polyenes are incorporated therebetween. Thus, the single-chain catalyst will produce a polymer fraction substantially free of long chain branching, while the multi-chain catalyst produces the long chain branched polymer fraction in the same reactor without gel formation and reactor fouling. Thus, the first reactor polyethylene product comprises a first fraction having long chain branching and a second fraction substantially free of long chain branching. As used herein, “substantially free of long chain branching” means less than 0.01 long chain branches per 1000 carbon atoms (LCBs/1000C) as measured by NMR. In the Examples below, the first reactor is called the high density reactor as the first reactor polyethylene product may have a density greater than 0.930 g/cc, and a melt index (I₂) greater than 3 dg/min. In one or more embodiments, the trimodal ethylene-based polymer comprises 35 to 55 wt.% of the first reactor polyethylene product comprising the first fraction and second fraction.

[0051] In one or more embodiments, the first fraction i.e., the long chain branched fraction may occupy about 2 to 10 wt.% of the multimodal ethylene-based polymer (e.g., the trimodal ethylene-based polymer).

[0052] The second reactor, which does not include an initial polyene feed and also does not include a multi-chain catalyst, produces a second reactor polyethylene product also substantially free of long chain branching. In this case, the single-chain catalyst in the second reactor will polymerize ethylene and optionally alpha-olefin comonomer. In one or more embodiments, the trimodal ethylene-based polymer comprises 45 to 65 wt.% of the second reactor polyethylene

product, which comprises at least the third polymer fraction. In the Examples below, the second reactor is called the low density reactor as the second reactor polyethylene product may have a density of less than 0.910 g/cc, a melt index (I_2) less than 0.8 dg/min, and an MWD less than 3.0. For the trimodal ethylene based-polymer, the combination of the first reactor (high density reactor) polyethylene product having the first fraction with long chain branching and the second fraction and the second reactor (low density reactor) having the third fraction polyethylene product yields a molecular weight distribution as depicted in FIG. 1.

[0053] *Films*

[0054] Additional embodiments of the present disclosure are directed to films. In some embodiments, the films may include multimodal ethylene-based polymers or trimodal ethylene-based polymers as described above.

[0055] In other embodiments, the film may comprise an ethylene-based polymer, which is the polymerized reaction product of ethylene, C_3 - C_{14} α -olefin monomer, and optionally polyene. In embodiments, this ethylene-based polymer may be multimodal and/or trimodal. In additional embodiments, the ethylene-based polymer of the film may comprise the polymerized reaction product of ethylene, C_3 - C_{14} α -olefin monomer, and polyene. In specific embodiments, the film may comprise at least 95 wt.% ethylene-based polymer, at least 97 wt.% ethylene-based polymer, at least 99 wt.% ethylene-based polymer, or at least 99.5 wt.% ethylene-based polymer. In further embodiments, the film is substantially free of any other polymeric component.

[0056] For these film embodiments, the film may comprise a normalized dart strength (DS) greater than or equal to $400 + 1400 / (MS - 2.7)$, wherein normalized DS is measured in gram (g) according to ASTM 1709 Method A divided by the film thickness in mils with the condition that melt strength (MS) is at least 4 cN. This relationship between normalized dart strength and melt strength is depicted in FIG. 2. By simultaneously achieving higher normalized dart strength and melt strength, the present films does not sacrifice abuse resistance performance for processibility, which is the tradeoff for LLDPE/LDPE blends. In further embodiments as also depicted in FIG. 2, the normalized DS is greater than or equal to $430 + 2000 / (MS - 2.4)$, greater than or equal to $400 + 2736 / (MS - 2.2)$, or greater than or equal to $390 + 3900 / (MS - 2.5)$. Moreover, the normalized DS of the film may be from 750 to 1750 g/mil, or from 750 to 1500 g/mil.

[0057] The films may comprise a monolayer film or multilayer film. 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 0.5 to 5 mils, from 1 to 4 mils, or from 1.5 to 2.5 mils.

[0058] Various methodologies are contemplated for producing the films of this disclosure. In one or more embodiments, the process of manufacturing the film may include cast film extrusion or blown film extrusion.

[0059] *Additives*

[0060] It should be understood that the above-described multimodal ethylene-based polymers, the trimodal ethylene-based polymers, or films produced therefrom 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, anti-block 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.

[0061] *Articles*

[0062] Embodiments of the present disclosure also relate to articles, such as packages, formed from the films of the present disclosure. The films of the present disclosure are particularly useful in articles where good tear strength and dart strength are desired. Examples of such articles can include flexible packages, pouches, stand-up pouches, and pre-made packages or pouches. Various methods of producing embodiments of articles from the films disclosed herein would be familiar to one of ordinary skill in the art.

TEST METHODS

[0063] The test methods include the following:

[0064] *Melt index*

[0065] Melt indices I_2 and I_{10} 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.

[0066] *Density*

[0067] 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.

[0068] *ASTM D1709 Dart Drop*

[0069] 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.

[0070] 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.

[0071] 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.

[0072] 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 approximately 2 mil thick.

[0073] *Instrumented Dart Impact*

[0074] Instrumented dart impact method is measured according to ASTM D7192 on plastic film specimens using an Instron CEAST 9350 impact tester. The test is conducted using 12.7 mm diameter tup with hemispherical head, 75 mm diameter clamping assembly with rubber faced grips. The instrument is equipped with an environmental chamber for testing at low or high temperature. Typical specimen size is 125 mm x 125 mm. Standard test velocity is 200 m/min.

[0075] *Gel Permeation Chromatography Size Exclusion Chromatography (SEC) (Conventional GPC)*

[0076] The GPC-SEC (Conventional GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

[0077] *Triple Detector GPC (TD) (Absolute GPC)*

[0078] The GPC-TD (Absolute GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

[0079] *MD Tear*

[0080] 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.

[0081] *Linear Viscoelastic Behavior (Small Amplitude Oscillatory Shear)*

[0082] Linear viscoelastic (LVE) behavior was measured in simple shear via a strain-controlled, separated motor-transducer ARES-G2 rheometer (TA Instruments) equipped with 25-mm parallel plates. Measurements were performed at 190 °C.

[0083] The geometry was contained in an insulated forced-convection oven (FCO) with a temperature control to within 0.1 °C, and nitrogen purge gas was used to prevent oxidative damage to the material. Small-amplitude oscillatory shear (SAOS) was used to characterize the LVE material response in simple shear. The experimental procedure in simple shear was as follows. The test specimen (25-mm diameter disk) was loaded and centered on the bottom plate previously brought to the testing temperature of 190 °C. Once the FCO temperature reading reached 190 ± 0.1 °C, the top plate was slowly lowered onto the specimen until contact. A small normal force ($\approx 1\text{--}2$ N) was maintained as the excess material at the edge of the parallel plates was quickly ($\leq \approx 20$ s) trimmed with a Hyde stiff brass scraper to achieve the proper disk-shape geometry. After trimming, the gap was slightly lowered (by $\leq \approx 0.03$ mm) to ensure complete filling of the parallel-plate geometry. The dwell time before testing, when temperature homogeneity was established and residual stresses were relaxed, was 180 s. To identify the range of strain amplitudes associated with the LVE response in shear, critical strains for the onset of NLVE behavior were determined by isochronal strain sweeps performed at four angular frequencies ($\omega = 0.1, 1, 10,$ and 100 rad/s).

[0084] Specimens were then subjected to a SAOS excitation in the frequency range 0.1–100 rad/s. During these isothermal frequency sweeps, the angular frequency ω was varied from high (100 rad/s) to low (0.1 rad/s) and the strain amplitude γ_0 was progressively increased (within the LVE regime and in the range 0.1–50%) with decreasing frequency of oscillation to comply with the resolution of the torque transducer at low frequencies.

[0085] An SAOS frequency sweep was performed on one test specimen for each material under study. The resulting data were analyzed in terms of the magnitude of the complex shear viscosity, $|\eta^*(\omega)| \equiv |G''(\omega)/\omega - iG'(\omega)/\omega|$, defined in terms of two frequency-dependent SAOS material functions: the storage shear modulus, $G'(\omega)$, and the loss shear modulus, $G''(\omega)$.

[0086] *ASTM D1922 MD (Machine Direction) and CD (Cross Direction) Elmendorf Tear Type B*

[0087] The Elmendorf Tear test determines the average force to propagate tearing through a specified length of plastic film or non-rigid sheeting, after the tear has been started, using an Elmendorf-type tearing tester.

[0088] After film production from the sample to be tested, the film was conditioned for at least 40 hours at 23 °C (+/- 2 °C) and 50% R.H (+/- 5) as per ASTM standards. Standard testing conditions were 23 °C (+/- 2 °C) and 50% R.H (+/- 5) as per ASTM standards.

[0089] The force, in grams, required to propagate tearing across a film or sheeting specimen was measured, using a precisely calibrated pendulum device. In the test, acting by gravity, the pendulum swung through an arc, tearing the specimen from a precut slit. The specimen was held on one side by the pendulum, and on the other side by a stationary member. The loss in energy by the pendulum was indicated by a pointer or by an electronic scale. The scale indication was a function of the force required to tear the specimen.

[0090] The sample specimen geometry used in the Elmendorf tear test was the 'constant radius geometry' as specified in ASTM D1922. Testing is typically carried out on specimens that have been cut from both the film MD and CD directions. Prior to testing, the film specimen thickness was measured at the sample center. A total of 15 specimens per film direction were tested, and the average tear strength and average thickness reported. The average tear strength was normalized to the average thickness.

EXAMPLES

[0091] 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.

[0092] *Polymer Synthesis*

[0093] Inventive Trimodal ethylene-based polymers **1-11**, which were produced by dual reactors having a multi-chain catalyst and two single-chain catalysts therein, were prepared by the method described below. Comparative Example **C1** was a bimodal ethylene-based polymer produced in a dual reactor system having a single-chain catalyst in each reactor but no multi-chain catalyst. Comparative Example **C2** was a bimodal ethylene-based polymer produced in a single reactor system having a single-chain catalyst and a multi-chain catalyst. Comparative Example **C3** was a unimodal ethylene-based polymer produced in a single reactor system having a single-chain catalyst.

[0094] All raw materials (monomer and comonomer) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, ISOPAR-E) were purified with molecular sieves before introduction into the reaction environment. Hydrogen was supplied pressurized as a high purity grade and was not further purified. The reactor monomer feed stream was pressurized via a mechanical compressor to above reaction pressure. The solvent and comonomer feed were pressurized via a pump to above reaction pressure. The individual catalyst components were manually batch diluted with purified solvent and pressured to above reaction pressure. All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems.

[0095] A two reactor system was used in a parallel configuration. Each continuous solution polymerization reactor consisted of a liquid full, non-adiabatic, isothermal, continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, diene, hydrogen, and catalyst component is possible. The total fresh feed stream to each reactor (solvent, monomer, comonomer, diene, and hydrogen) was temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The catalyst components were directly injected into the polymerization reactor. The primary catalyst component feed was computer controlled to maintain each reactor monomer conversion at the specified targets. The cocatalyst components were fed based on calculated specified molar ratios to the primary catalyst component. Reactor feeds are shown in Tables 1A and 1B. Immediately following the reactor feed injection location, the feed stream was mixed with the circulating polymerization reactor contents with static mixing elements. The reactor had an oil jacket around responsible for maintaining an isothermal reaction environment at the specified temperature.

[0096] In dual parallel reactor configuration, the effluent from each polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exited the appropriate reactor and were blended. The contents were deactivated with the addition of isopropanol. At this same reactor exit location, other additives were added for polymer stabilization (typical antioxidants suitable for stabilization during extrusion and film fabrication).

[0097] Following catalyst deactivation and additive addition, the reactor effluent entered a devolatilization system where the polymer is removed from the non-polymer stream. The isolated

Example		C1	1	2	3	4	5	C2
		A	A	A	A	A	A	A
Rx2 Co-Catalyst 2 Type	Type	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B
Rx2 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Rx2 Co-Catalyst 2 to Catalyst Molar Ratio (A1 to Catalyst Metal ratio)	Ratio	40.7	10.8	10.1	8.3	7.2	5.9	5.6
Rx2 Residence Time	Min	12.7	12.7	12.6	12.6	12.7	12.6	12.5
Rx2 Production Split	wt. %	45.17	45.54	46.05	46.39	46.29	46.69	100.00

[0099] Table 1B

Example		C3	6	7	8	9	10	11
Reactor Configuration	Type	Single	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel
Comonomer type	Type	Octene	Octene	Octene	Octene	Octene	Octene	Octene
Low Density Reactor (Rx1)								
Rx1 Feed Solvent / Ethylene Mass Flow Ratio	g/g	8.4	8.4	8.5	8.4	8.5	8.4	8.4
Rx1 Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.08	0.07	0.07	0.07	0.06	0.06	0.06
Rx1 Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.2E-04	1.1E-04	1.1E-04	1.1E-04	1.1E-04	1.1E-04	1.1E-04
Rx1 Temperature	°C	160	160	160	160	160	160	160
Rx1 Pressure	Barg	28	28	28	28	28	28	28
Rx1 Ethylene Conversion	%	83.2	83.1	83.3	83.2	82.9	83.1	83.2
Rx1 Catalyst-A Type	Type	Cat A	Cat A	Cat A	Cat A	Cat A	Cat A	Cat A
Rx1 Co-Catalyst 1 Type	Type	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A
Rx1 Co-Catalyst 2 Type	Type	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B
Rx1 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.2	1.2	1.0	1.1	1.3	1.3	1.2
Rx1 Co-Catalyst 2 to Catalyst Molar Ratio (A1 to Catalyst Metal ratio)	Ratio	58.1	47.5	44.5	46.8	37.7	35.7	36.5
Rx1 [Al] from Co-Catalyst 2	Ppmw	0.93	0.93	0.93	0.93	0.76	0.76	0.76
Rx1 Residence Time	Min	8.3	8.3	8.3	8.3	6.8	6.8	6.8
Percentage of Total Ethylene Feed to Rx1	wt. %		52.4%	52.3%	52.3%	57.3%	57.3%	57.3%
Rx1 Production Split	wt. %	100.00	43.56	43.63	54.56	59.38	59.77	59.76
High Density Reactor (Rx2)								
Rx2 Feed Solvent / Ethylene Mass Flow Ratio	g/g		7.6	7.6	7.6	7.5	7.5	7.5
Rx2 Feed Comonomer / Ethylene Mass Flow Ratio	g/g		0.175	0.168	0.168	0.166	0.135	0.135
Rx2 Feed Hydrogen /	g/g		1.2E-04	1.3E-04	1.0E-04	1.1E-04	1.1E-04	1.4E-04

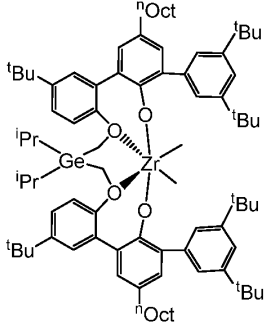
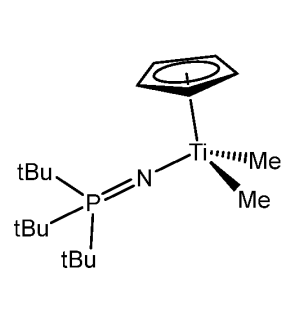
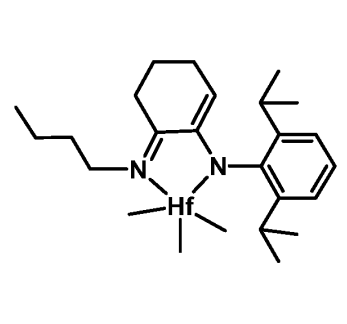
Ethylene Mass Flow Ratio								
Rx2 Feed Ethylene/Pentadiene Mass Flow Ratio	g/g		3791	3791	1314	1369	2116	2104
Rx2 Temperature	°C		150	150	150	150	150	150
Rx2 Pressure	Barg		28	28	28	28	28	28
Rx2 Ethylene Conversion	%		88.5	88.4	90.3	90.2	90.3	90.3
Rx2 Catalyst 1 Type	Type		Cat B	Cat B	Cat B	Cat B	Cat B	Cat B
Rx2 Catalyst 2 Type	Type		Cat C	Cat C	Cat C	Cat C	Cat C	Cat C
Rx2 Co-Catalyst 1 Type	Type		CoCat A	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A
Rx2 Co-Catalyst 2 Type	Type		CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B
Rx2 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio		1.2	1.2	1.2	1.2	1.2	1.2
Rx2 Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio		6.1	5.3	6.1	12.9	11.4	8.3
Rx2 Residence Time	Min		14.5	14.4	12.5	12.6	12.7	12.6
Rx2 Production Split	wt.%	0.00	43.56	43.63	45.44	40.62	40.23	40.24

[00100] Co-catalyst A (CoCat A is bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate

[00101] Co-catalyst B (CoCat B) is MMAO-3A or modified methyl aluminoxane

[00102] The structures for CAT A, CAT B, and CAT C, which are noted in Tables 1A and 1B, are provided in Table 2 as follows.

[00103] Table 2

		
Catalyst A (Cat A)	Catalyst B (Cat B)	Catalyst C (Cat C)

[00104] *Film Processing*

[00105] Films were run utilizing Inventive Examples 1-11, Comparative Example C1 and the commercial resins and blends C4-C7.

[00106] C4 comprised 80 wt. % C1 and 20 wt.% AGILITY™ 1021. AGILITY™ 1021, which is commercially available from Dow Inc., Midland MI, is an LDPE resin having a density of 0.919 g/cc and a melt index (I₂) of 1.9 dg/min.

[00107] C5 comprised 100 wt.% of a comparative bimodal polyethylene resin having a density of 0.918 g/cc and a melt index (I₂) of 0.85 dg/min. The comparative bimodal polyethylene resin was produced according to the methodology of Inventive Example 1 of PCT Publication WO2015200742, which is incorporated by reference herein.

[00108] C6 comprised 90 wt.% C5 and 10 wt.% AGILITY™ 1021.

[00109] C7 comprised 80 wt.% C5 and 20 wt.% AGILITY™ 1021.

[00110] Specifically, 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.

[00111] *Film and Polymer Data*

[00112] Table 3A

Example		C1	1	2	3	4	5	C2
Polymer and Film Properties								
I ₂	dg/min	0.77	0.72	0.89	0.88	0.81	0.82	29.5
I10	dg/min	5.04	6.16	7.32	8.33	6.31	6.72	
I10/I ₂	Ratio	6.5	8.6	8.2	9.5	7.8	8.2	
Density	g/cm ³	0.916	0.919	0.917	0.917	0.917	0.916	0.935
Melt strength	cN	3.2	9.9	12.3	13.2	12.0	13.3	2.2
Extensibility	mm/s	147	133	133	129	134	126	178
V0.01	Pa s	8,981	8,182	8,981	9,176	10,358	12,385	
V0.1	Pa s	8,738	7,333	7,725	7,754	8,517	9,673	
V100	Pa s	2,232	1,543	1,502	1,462	1,532	1,551	
V500	Pa s	941	633	603	582	608	596	
Rheology ratio (V0.1/V100)	Ratio	3.9	4.8	5.1	5.3	5.6	6.2	
Mn SEC	kg/mol	42	30	28	27	28	26	16

Example		C1	1	2	3	4	5	C2
Mw SEC	kg/mol	112	105	105	106	107	108	54
Mp - SEC	kg/mol	79	54	49	47	49	42	30
Mz - SEC	kg/mol	222	254	268	282	281	296	316
Mw/Mn – SEC	Ratio	2.7	3.5	3.7	3.9	3.8	4.2	3.5
Mn TD	kg/mol	52	31	30	29	30	25	16
Mw TD	kg/mol	132	110	117	116	120	123	51
Mw/Mn TD	Ratio	2.5	3.6	3.9	4.1	4.0	5.0	3.2
Mw TD / Mw SEC	Ratio	1.18	1.05	1.12	1.10	1.12	1.14	0.94
g' avg	Ratio	0.85	1.00	0.88	0.90	0.91	0.91	0.99
IDI total E	J	5.1	3.2	3.8	3.3	5.1	5.7	
CD tear	gf	1,064	859	899	800	877	826	
est Elmendorf CD	gf	782	632	661	588	645	607	
MD tear	gf	720	516	569	517	582	524	
est Elmendorf MD	gf	529	379	418	380	428	385	
Haze	%	9	22	14	17	17	22	
Melt strength	cN	3.2	9.9	12.3	13.2	12.0	13.3	2.2
Dart A	g	1,800	1,710	1,815	1,710	2,025	2,055	
Normalized Dart	g/mil	857	760	807	834	942	979	
film thickness	mil	2.10	2.25	2.25	2.05	2.15	2.10	
400 + 1400 / (MS - 2.7)	g/mil	3200	594	546	533	551	532	
430 + 2000 / (MS - 2.4)	g/mil	2930	697	632	615	638	613	
400 + 2736 / (MS - 2.2)	g/mil	3136	755	671	649	679	646	
390 + 3900 / (MS - 2.5)	g/mil	5961	917	788	754	801	751	

[00113] Table 3B

Example		C3	6	7	8	9	10	11
Polymer and Film Properties								
I2	dg/min	0.26	0.89	0.92	0.88	0.76	0.78	0.84
I10	dg/min	1.42	7.16	7.52	7.01	5.53	5.65	6.22
I10/I2	Ratio	5.5	8.0	8.2	8.0	7.3	7.2	7.4
Density	g/cm ³	0.8999	0.917	0.919	0.919	0.916	0.918	0.918
melt strength	cN	4.5	6.1	5.9	6.5	5.3	4.6	4.7
Extensibility	mm/s	67	162	153	144	245	>250	>250
V0.01	Pa s		10,324	10,269	10,483	11,468	10,785	10,266
V0.1	Pa s		8,868	8,811	8,941	10,523	10,021	9,777
V100	Pa s		1,598	1,553	1,631	1,943	1,910	1,608
V500	Pa s		625	597	659	747	763	564
Rheology ratio (V0.1/V100)	Ratio		5.5	5.7	5.5	5.4	5.2	6.1
Mn SEC	kg/mol	71	28	25	30	32	33	28
Mw SEC	kg/mol	144	109	106	110	113	113	112
Mp - SEC	kg/mol	113	49	43	52	60	59	50
Mz - SEC	kg/mol	244	292	287	306	259	263	277
Mw/Mn – SEC	ratio	2.0	3.9	4.2	3.7	3.5	3.5	4.0
Mn TD	kg/mol	85	30	28	33	34	36	30
Mw TD	kg/mol	166	119	119	125	130	126	119
Mw/Mn TD	Ratio	1.9	3.9	4.2	3.8	3.8	3.6	3.9
Mw TD / Mw SEC	Ratio	1.15	1.09	1.12	1.14	1.14	1.11	1.06
g' avg	Ratio	0.86	0.88	0.89	0.89	0.89	0.89	0.91
IDI total E	J		2.6	1.8	6.5	8.2	7.9	6.0
CD tear	gf		944	964	962	870	892	871
est Elmendorf CD	gf		694	709	708	640	656	640
MD tear	gf		582	506	559	505	534	464

Example		C3	6	7	8	9	10	11
est Elmendorf MD	gf		428	372	411	371	392	341
Haze	%		11	12	11	8	8	9
melt strength	cN	4.5	6.1	5.9	6.5	5.3	4.6	4.7
Dart A	g		2,112	2,256	2,448	2,952	2,808	2,916
normalized Dart	g/mil		1,006	1,049	1,139	1,373	1,306	1,356
film thickness	mil		2.10	2.15	2.15	2.15	2.15	2.15
400 + 1400 / (MS - 2.7)	g/mil		812	838	768	938	1137	1100
430 + 2000 / (MS - 2.4)	g/mil		971	1001	918	1120	1339	1300
400 + 2736 / (MS - 2.2)	g/mil		1102	1139	1036	1283	1540	1494
390 + 3900 / (MS - 2.5)	g/mil		1473	1537	1365	1783	2247	2163

[00114] Table 3C

Example		C4	C5	C6	C7
Polymer and Film Properties					
I2	dg/min		0.85		
Density	g/cm ³		0.918		
Melt strength	cN	15.0	4.4	11.3	15.3
IDI total E	J	0.8	2.4	1.2	0.8
CD tear	gf	1,661	1,271	1,560	1,813
est Elmendorf CD	gf	1,222	934	1,147	1,333
MD tear	gf	712	730	766	704
est Elmendorf MD	gf	524	537	564	518
Haze	%	6.0	10.6	7.5	7.3
melt strength	cN	16.0	4.4	11.3	16.3
Dart A	G	504	1,335	888	558
normalized Dart	g/mil	234	621	413	254
film thickness	mil	2.15	2.15	2.15	2.20
400 + 1400 / (MS - 2.7)	g/mil	505	1224	563	503
430 + 2000 / (MS - 2.4)	g/mil	577	1430	655	574
400 + 2736 / (MS - 2.2)	g/mil	598	1644	701	594
390 + 3900 / (MS - 2.5)	g/mil	679	2443	833	673

[00115] As shown in Tables 3A-3C, inventive samples 1-11 had melt strengths ranging from 4.7 to 13.3 cN, and Normalized Dart A of 760 to 1373 g/mil. These Normalized Dart A values are significantly higher than the blends of C4, C6, and C7, which included LDPE to boost the melt strength, as well as the C5 single resin film. This demonstrates how LDPE increases melt strength and processibility, but at the tradeoff of significantly reducing the abuse resistance i.e., the Normalized Dart A.

[00116] Moreover, as shown in Comparative Example C1, which did not include a multi-chain catalyst or diene, the melt strength was lower (3.2 cN) due to lack of long chain branching. Moreover, the first reactor bimodal polymer (Comparative Example C2) has long chain branching present but cannot achieve the melt strength (2.2 cN) of the inventive polymers due to the high

melt index (I_2 of 29.5 dg/min). Finally, unimodal Comparative Example **C3** is essentially free of long chain branching and has a melt strength of 4.5 cN but it is achieved by having a very low melt index (I_2) of 0.26 dg/min.

[00117] Having described the subject matter of the present disclosure in detail and by reference to specific embodiments, it is noted that the various details disclosed in the present disclosure should not be taken to imply that these details relate to elements that are essential components of the various embodiments described in the present disclosure. Further, it will be apparent that modifications and variations are possible without departing from the scope of the present disclosure, including, but not limited to, embodiments defined in the appended claims.

CLAIMS

1. A process for producing ethylene-based polymer in a reactor system comprising a first reactor and a second reactor, the process comprising:

polymerizing ethylene, one or more (C₃-C₁₄) α -olefin monomers, and at least one polyene, in the presence of one multi-chain catalyst and at least one single-chain catalyst in the first reactor to produce a first reactor polyethylene product comprising long chain branching, wherein the multi-chain catalyst comprises a plurality of polymerization sites, and wherein the long-chain branching occurs by connecting two polymer chains of the multi-chain catalyst with the polyene in a concerted fashion during the polymerization; and

polymerizing ethylene and one or more (C₃-C₁₄) α -olefin monomers in the absence of an initial polyene feed and in the presence of at least one single-chain catalyst in the second reactor to produce a second reactor polyethylene product,

wherein the ethylene-based polymer comprises the first and second reactor polyethylene products.

2. The process of claim 1, wherein solution polymerization is conducted in the first reactor, the second reactor, or both.

3. The process of any preceding claim, wherein the at least one single-chain catalyst in the first reactor, the second reactor, or both comprises a phosphinimine catalyst.

4. The process of any preceding claim, wherein the at least one single-chain catalyst in the first reactor, the second reactor, or both comprises a bis(biphenylphenoxy)catalyst.

5. The process of any preceding claim, wherein the ethylene-based polymer comprises from 35 to 55 wt% of the first reactor polyethylene product and 45 to 65 wt% of the second reactor polyethylene product.

6. The process of any preceding claim, wherein the second reactor polyethylene product has a density of less than 0.910 g/cc, a melt index (I₂) less than 0.8 dg/min as measured according to ASTM D1238 (2.16 Kg/190 °C), and a molecular weight distribution (MWD) less than 3.0 as

measured according to Gel Permeation Chromatography (GPC).

7. The process of any preceding claim, wherein the first reactor polyethylene product has a density greater than 0.930 g/cc, and a melt index (I_2) greater than 5.0 dg/min.
8. The process of any preceding claim, wherein the multi-chain catalyst produces a long chain branched fraction of less than 10 wt.% of the ethylene-based polymer.
9. The process of any preceding claim, wherein the ethylene-based polymer has a melt strength (MS) from 4.0 to 25.0 cN, wherein 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).
10. The process of claim 9, wherein the melt strength (MS) is from 8.0 to 15 cN.
11. The process of any preceding claim, wherein the ethylene-based polymer has a rheology ratio $V_{0.1}/V_{100}$ from 4.0 to 12.0, 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, and
12. The process of claim 11, wherein the rheology ratio $V_{0.1}/V_{100}$ is from 4.0 to 8.0.
13. The process of any preceding claim, wherein the ethylene-based polymer has an I_2 of 0.5 to 2.0 dg/min.