

POLYMER BLENDS COMPRISING TRIMODAL ETHYLENE-BASED
POLYMERS AND PCR

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/579,100 filed August 28, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments are generally related to multimodal ethylene-based polymers and are particularly related to polymer blends comprising trimodal ethylene-based polymers and post-consumer recycled (PCR) ethylene-based polymers.

BACKGROUND

[0003] PCR films have inferior abuse properties compared to most virgin polyethylene films due to contamination and excessive thermal history associated with the recycling process. These inferior abuse properties make it challenging to upcycle PCR polymers into high-end film applications at meaningful concentrations of PCR. Instrumented dart impact (IDI) resistance is one abuse property where PCR films lag behind virgin films.

[0004] Accordingly, there is a need for films, which meet the desired abuse standards (including IDI), while still incorporating meaningful amounts of PCR for improved sustainability.

SUMMARY

[0005] Embodiments of the present disclosure meet this need by providing polymer blends including PCR ethylene-based polymer and a trimodal ethylene-based polymer. Without being limited by theory, the introduction of the trimodal ethylene-based polymer allows the film to incorporate meaningful amounts of PCR ethylene-based polymer while still maintaining the desired abuse properties (such as instrumented dart impact resistance).

[0006] According to one or more embodiments, polymer blends comprising PCR ethylene-based polymer and trimodal ethylene-based polymer are provided. The trimodal ethylene-based polymer comprises 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.

[0007] These and other embodiments are described in more detail in the following Detailed Description.

DETAILED DESCRIPTION

Definitions

[0008] 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 monomer types.

[0009] “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 monomer types). 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).

[0010] 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.

[0011] 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.

[0012] “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.

[0013] “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).

[0014] 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.

[0015] 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.

[0016] The term “defect” refers to a visible defect in the bulk polymer or film. Defects may arise from foreign contamination or degraded polymer. When defects are present, they reduce transparency in the film.

[0017] 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.

[0018] 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.

[0019] “Recycled polymer” refers to polymers, which were incorporated into products and subsequently re-melted to form a recycled polymer. The term “recycled polymer” refers to mechanically recycled polymers, where the polymer is melted and reincorporated into a new product. “Recycled polymer” does not include chemically recycled polymers, where the polymer is broken down into constituent monomers and incorporated into a new virgin polymer. The term “recycled polymer” embraces both pre-consumer recycled polymer and post-consumer recycled polymer. Recycled polymers are defined in ISO 14021 7.8.1.1.

[0020] The terms “pre-consumer recycled polymer” and “post-industrial recycled polymer” refer to polymers, including blends of polymers, recovered from pre-consumer material, as defined by ISO-14021. The generic term pre-consumer recycled polymer thus includes blends of polymers recovered from materials diverted from the waste stream during a manufacturing process. The generic term pre-consumer recycled polymer excludes the reutilization of materials,

such as rework, regrind, or scrap, generated in a process and capable of being reclaimed within the same process that generated it. Pre-consumer recycled polymer is defined in ISO 14021 7.8.1.1.

[0021] The term “post-consumer recycled” (or “PCR”), as used herein, refers to a polymeric material that includes materials previously used in a consumer or industry application (i.e., pre-consumer recycled polymer and post-industrial recycled polymer). PCR is typically collected from recycling programs and recycling plants. The PCR ethylene-based polymer may include one or more of ethylene-based polymers, such as LDPE, LLDPE, HDPE, or polyethylene. The PCR may include one or more contaminants. The contaminants may be the result of the polymeric material’s use prior to being repurposed for reuse. For example, contaminants may include paper, ink, food residue, or other recycled materials in addition to the polymer, which may result from the recycling process. PCR is distinct from virgin polymeric material. A virgin polymeric material (such as a virgin polyethylene resin) does not include materials previously used in a consumer or industry application. Virgin polymeric material has not undergone, or otherwise has not been subject to, a heat process or a molding process, after the initial polymer manufacturing process. The physical, chemical, and flow properties of PCR resins differ when compared to virgin polymeric resin, which in turn can present challenges to incorporating PCR into formulations for commercial use. Post-consumer resin is defined in ISO 14021 7.8.1.1.

Polymer Blends

[0022] Embodiments of the present disclosure are directed polymer blends comprising a post-consumer recycled (PCR) ethylene-based polymer; and a trimodal ethylene-based polymer. In embodiments, the polymer blend may comprise at least 80 wt. %, such as at least 90 wt. %, at least 95 wt. %, at least 99 wt. %, or even at least 99.9 wt. % of the combined weight of the PCR ethylene-based polymer and the trimodal ethylene-based polymer, on the basis of the total weight of the polymer blend.

[0023] The polymer blend may comprise 20 to 50 wt.% of the PCR ethylene-based polymer. In embodiments, the polymer blend may comprise 20 wt. % to 45 wt. %, 20 wt. % to 40 wt. %, 30 wt. % to 50 wt. %, 35 wt. % to 50 wt. %, 40 wt. % to 50 wt. %, or any subset thereof of the PCR ethylene-based polymer, on the basis of the total weight of the polymer blend. The remainder of the PCR ethylene-based polymer may comprise the trimodal ethylene-based polymer.

PCR Ethylene-Based Polymer

[0024] The PCR ethylene-based polymer may comprise at least 51 wt. % of post-consumer material, such as at least 75 wt. %, at least 80 wt. %, at least 85 wt. %, at least 90 wt. %, at least 95 wt. %, or even at least 99 wt. % of post-consumer material, on the basis of the total weight of the PCR ethylene-based polymer.

[0025] The PCR ethylene-based polymer may comprise an LDPE, an HDPE, an LLDPE, or a blend thereof. In embodiments, the PCR ethylene-based polymer resin comprise at least 50 wt. %, at least 75 wt. %, at least 85 wt. %, at least 90 wt. %, at least 95 wt. %, or even at least 99 wt. % of an LDPE, an HDPE, an LLDPE, or a blend thereof, on the basis of the total weight of the PCR ethylene-based polymer.

[0026] The PCR ethylene-based polymer may have a density of 0.900 to 0.930 g/cc. In embodiments, the PCR ethylene-based polymer may have a density of from 0.900 to 0.925 g/cc, 0.900 to 0.920 g/cc, 0.900 to 0.915 g/cc, 0.900 to 0.910 g/cc, 0.905 to 0.930 g/cc, 0.910 to 0.930 g/cc, 0.915 to 0.930 g/cc, 0.920 to 0.930 g/cc, 0.905 to 0.925 g/cc, 0.910 to 0.920 g/cc, or any subset thereof.

[0027] The PCR ethylene-based polymer may have a melt index (I_2) of 0.5 to 3 dg/min. In embodiments, the PCR ethylene-based polymer may have a melt index (I_2) of 0.5 to 2.5 dg/min, 0.5 to 2.0 dg/min, 0.5 to 1.5 dg/min, 0.5 to 1.0 dg/min, 1 to 3 dg/min, 1.5 to 3 dg/min, 2 to 3 dg/min, 2.5 to 3 dg/min, 1 to 2.5 dg/min, or any subset thereof.

Trimodal Ethylene-based Polymers

[0028] The polymer blend includes trimodal ethylene-based polymers. It has been surprisingly found that the combination of trimodal ethylene-based polymers and PCR ethylene-based polymers causes improved instrumented dart impact (IDI) at a given PCR content.

[0029] The trimodal ethylene-based polymers comprise 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.

[0030] 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.

[0031] The C₃-C₁₄ alpha-olefin comonomer may include one or more of 1-propylene, 1-butene, 1-hexene, 1-octene, or combinations thereof.

[0032] 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.

[0033] 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 long chain branching.

[0034] The trimodal ethylene-based polymer may have a melt index (I_2) of 0.3 to 3 dg/min, such as from 0.3 to 2 dg/min, from 0.3 to 1 dg/min, from 0.5 to 3 dg/min, from 0.5 to 2 dg/min, from 0.5 to 1.0 dg/min, or from 0.7 to 0.9 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 5.0 to 15.0, or from 5.0 to 10.0.

[0035] In one or more embodiments, the trimodal ethylene-based polymer has a density of 0.910 to 0.930 g/cc, such as from 0.910 to 0.925 g/cc, from 0.910 to 0.920 g/cc, or from 0.912 to 0.920 g/cc.

[0036] In one or more embodiments, the trimodal ethylene-based polymer has a molecular weight distribution (MWD) of 3.0 to 5.0, 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.

Production of the Trimodal Ethylene-Based Polymer

[0037] 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.

[0038] 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

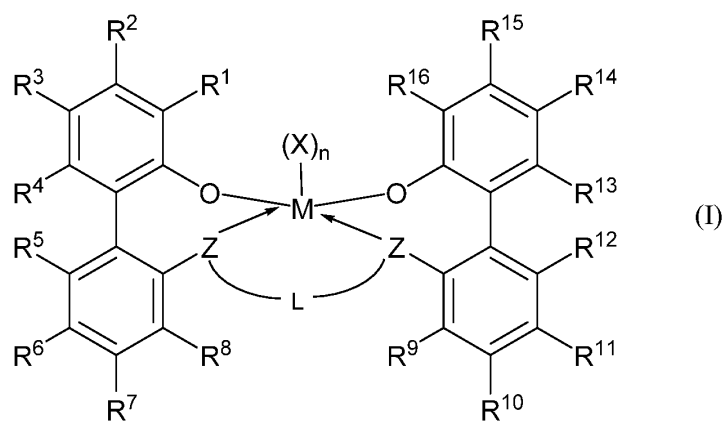
reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0039] 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.

[0040] 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.

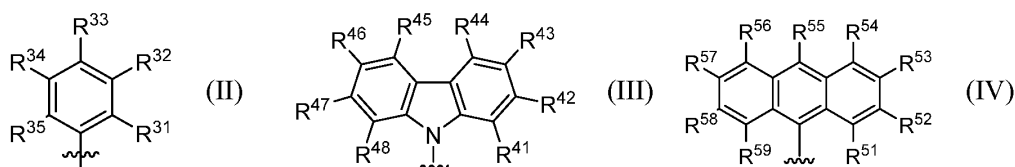
[0041] As used herein, “single-chain catalyst” is a polymerization catalyst having one active polymerization site and/or reactive metal center and one active polymer chain on that site. Various single-chain catalysts are considered suitable. These may include bis-metallocene catalysts, phosphinimine, 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).

[0042] 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):



[0043] 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, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):

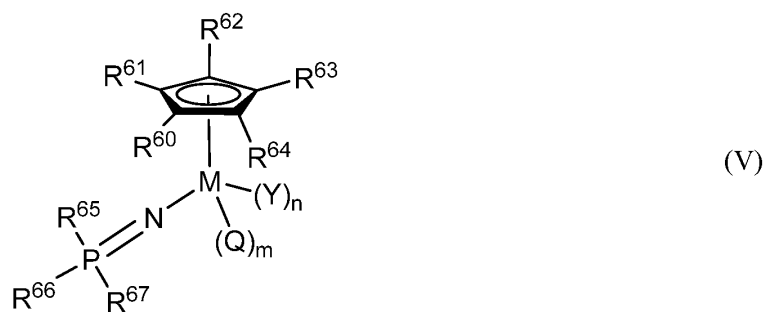


[0044] In formulas (II), (III), and (IV), each of R³¹⁻³⁵, R⁴¹⁻⁴⁸, and R⁵¹⁻⁵⁹ is independently chosen from $-\text{H}$, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen, provided at least one of R¹ or R¹⁶ is a radical having formula (II), a radical having formula (III), or a radical having formula (IV).

[0045] In one or more embodiments, each X can be a monodentate ligand that, independently from any other ligands X, is a halogen, unsubstituted (C₁-C₂₀)hydrocarbyl, unsubstituted (C₁-C₂₀)hydrocarbylC(O)O-, or R^KR^LN-, wherein each of R^K and R^L independently is an unsubstituted(C₁-C₂₀)hydrocarbyl.

[0046] 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.

[0047] 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):

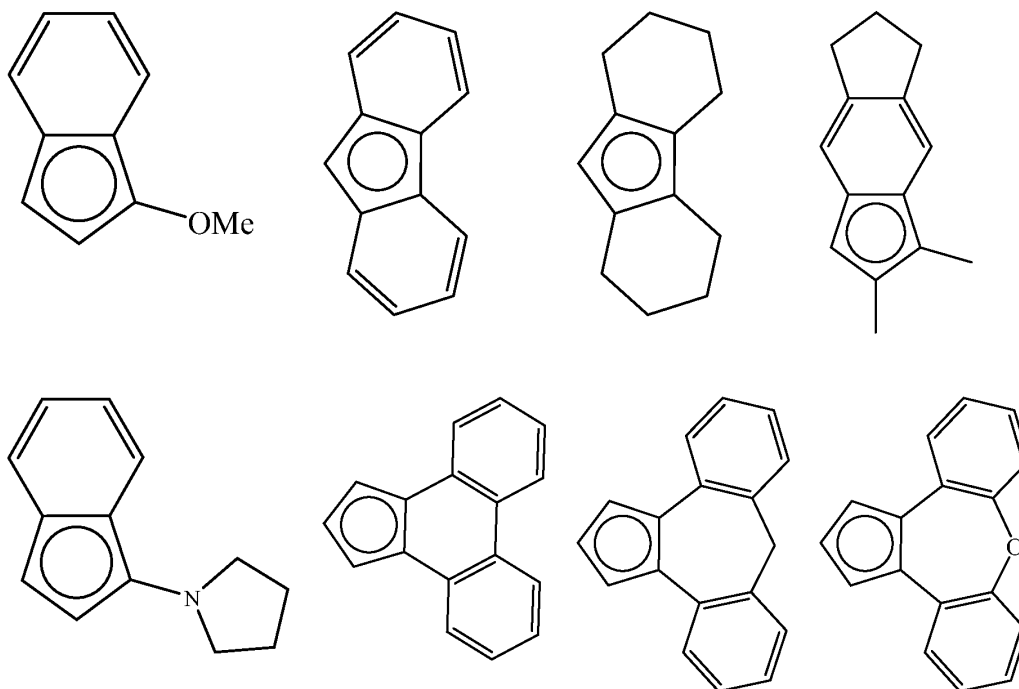


[0048] In formula (V), each Q is a monodentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, –CH₂Si(R^C)_{3-Q}(OR^C)_Q, –Si(R^C)_{3-J}(OR^C)_J, –OSi(R^C)_{3-J}(OR^C)_J, –CH₂Ge(R^C)_{3-J}(OR^C)_J, –Ge(R^C)_{3-J}(OR^C)_J, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –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 metallocycle ring

[0049] 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.

[0050] 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.

[0051] 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:



[0052] 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 chains, 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 separate propagating 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.

[0053] 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.

[0054] 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).

[0055] 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 (I₂) less than 0.8 dg/min, and an MWD less than 3.0.

Films

[0056] Additional embodiments of the present disclosure are directed to films comprising these polymer blends. 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, from 1 to 3 mils, or from 1.5 to 2.5 mils.

[0057] 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.

Additives

[0058] It should be understood that the above-described polymer blends, 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. In embodiments, the polymer blends may comprise from 0 wt. % to 40 wt. %, such as from 0 wt. % to 15 wt. %, from 0 wt. % to 10 wt. %, from 0 wt. % to 5 wt. %, from 0.01 wt. % to 40 wt. %, from 0.01 wt. % to 15 wt. %, from 0.01 wt. % to 10 wt. %, from 0.01 wt. % to 5 wt. %, from 0.1 wt. % to 40 wt. %, from 0.1 wt. % to 15 wt. %, from 0.1 wt. % to 10 wt. %, from 0.1 wt. % to 5 wt. %, from 1 wt. % to 40 wt. %, from 1 wt. % to 15 wt. %, from 1 wt. % to 10 wt. %, from 1 wt. % to 5 wt. %, or any subset thereof of the one or more additives, on the basis of the total polymer weight of the blend.

Articles

[0059] 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

[0060] The test methods include the following:

Melt Index

[0061] Melt indices I2 and I10 of polymer samples were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively.

Density

[0062] 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.

Instrumented Dart Impact

[0063] Instrumented dart impact is measured on a 6-inch x 6-inch square sample. The IDI dart test is based on ASTM D7192. The thickness of the film is measured at the sample center and the film is then clamped to give a 3-inch diameter unsupported test region. The film is struck by an impactor at the specimen center and perpendicular to the plane of the film. The impactor consists of a stainless-steel plunger rod 12.7 +/- 0.13 mm in diameter with a hemispherical end of the same diameter, with the end polished to a mirror finish. The impactor strikes the film specimen at 3.3 m/s with sufficient energy that at the end of the test the reduction in speed is less than 20%. From the force versus displacement curves, peak force, peak energy, peak and total displacement, and total energy are reported. Typically, ten replicates are measured and the average and standard deviation of the results reported.

Gel Permeation Chromatography Size Exclusion Chromatography (SEC) (Conventional GPC)

[0064] The GPC-SEC (Conventional GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

Triple Detector GPC (TD) (Absolute GPC)

[0065] The GPC-TD (Absolute GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

Dynamic Mechanical Spectroscopy (DMS)

[0066] The DMS measurements were performed according to the test procedure defined in PCT Publication WO2019067239A1.

Melt Strength (MS)

[0067] The DMS measurements were performed according to the test procedure defined in PCT Publication WO2019067239A1.

EXAMPLES

[0068] 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.

Materials

[0069] Trimodal ethylene-based polymers **S-1 to S-3**, which were produced in a dual reactor system with a multi-chain catalyst and two single-chain catalysts. Comparative Example **CS-A** 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. The synthesis conditions are described in Table 1.

[0070] 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.

[0071] The reactor configuration used was a dual reactor in parallel mode. Each reactor was 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 Table 1. The feed stream was continuously mixed with the reactor contents with the reactor agitator. The reactor had an oil jacket around responsible for maintaining an isothermal reaction environment at the specified temperature.

[0072] 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 introduced for polymer stabilization (these additives included typical antioxidants suitable for stabilization during extrusion and film fabrication).

[0073] Following catalyst deactivation and additive addition, the reactor effluent entered a devolatilization system where the polymer was removed from the non-polymer stream. The isolated polymer melt was pelletized and collected. There was no recycle in this process, but in general recycle can be achieved.

Table 1A

Example		CS-A	S-1	S-2	S-3
Reactor Configuration	Type	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel
Comonomer type	Type	Octene	Octene	Octene	Octene
Low Density Reactor (Rx1)					
Rx1 Feed Solvent / Ethylene Mass Flow Ratio	g/g	8.5	8.5	8.4	8.4
Rx1 Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.08	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
Rx1 Temperature	°C	160	160	160	160
Rx1 Pressure	Barg	28	28	28	28
Rx1 Ethylene Conversion	%	82.9	82.9	83.1	83.2
Rx1 Catalyst-A Type	Type	Cat A	Cat A	Cat A	Cat A
Rx1 Co-Catalyst 1 Type	Type	CoCat A	CoCat A	CoCat A	CoCat A
Rx1 Co-Catalyst 2 Type	Type	CoCat B	CoCat B	CoCat B	CoCat B

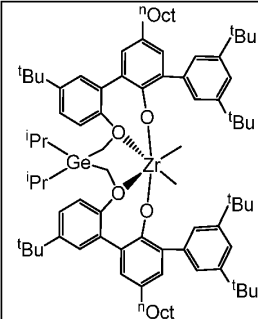
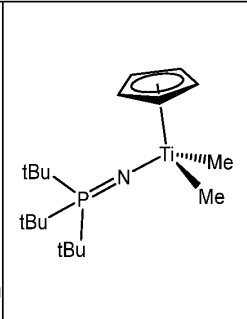
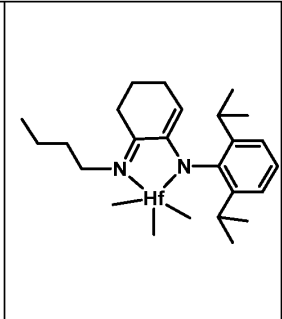
Rx1 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.0	1.3	1.3	1.2
Rx1 Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	54.6	37.7	35.7	36.5
Rx1 [Al] from Co-Catalyst 2	Ppmw	0.93	0.76	0.76	0.76
Rx1 Residence Time	Min	8.3	6.8	6.8	6.8
Percentage of Total Ethylene Feed to Rx1	wt. %	52.3%	57.3%	57.3%	57.3%
Rx1 Production Split	wt. %	54.8	59.4	59.8	59.8
High Density Reactor (Rx2)					
Rx2 Feed Solvent / Ethylene Mass Flow Ratio	g/g	7.5	7.5	7.5	7.5
Rx2 Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.124	0.166	0.135	0.135
Rx2 Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	8.4E-05	1.1E-04	1.1E-04	1.4E-04
Rx2 Feed Ethylene/Pentadiene Mass Flow Ratio	g/g		1369	2116	2104
Rx2 Temperature	°C	150	150	150	150
Rx2 Pressure	Barg	28	28	28	28
Rx2 Ethylene Conversion	%	90.3	90.2	90.3	90.3
Rx2 Catalyst 1 Type	Type	Cat B	Cat B	Cat B	Cat B
Rx2 Catalyst 2 Type	Type	None	Cat C	Cat C	Cat C
Rx2 Co-Catalyst 1 Type	Type	CoCat A	CoCat A	CoCat A	CoCat A
Rx2 Co-Catalyst 2 Type	Type	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
Rx2 Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	40.7	12.9	11.4	8.3
Rx2 Residence Time	Min	12.7	12.6	12.7	12.6
Rx2 Production Split	wt. %	45.2	40.6	40.2	40.2

[0074] Co-catalyst A (CoCat A is bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate

[0075] Co-catalyst B (CoCat B) is MMAO-3A or modified methyl aluminoxane

[0076] The structures for Cat A, Cat B, and Cat C, which are noted in Tables 1A and 1B, are provided in Table 2.

Table 2

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

[0077] Properties of CS-A, CS-C, and S1-S3 are shown in Table 3.

Table 3

Example		CS-A	S-1	S-2	S-3	CS-C
I ₂	dg/min	0.77	0.76	0.78	0.84	0.85
I ₁₀	dg/min	5.04	5.53	5.65	6.22	
I ₁₀ /I ₂	Ratio	6.5	7.3	7.2	7.4	
Density	g/cm ³	0.916	0.916	0.918	0.918	0.918
Melt strength	cN	3.2	5.3	4.6	4.7	4.4
Extensibility	mm/s	147	245	>250	>250	
V0.01	Pa s	8,981	11,468	10,785	10,266	
V0.1	Pa s	8,738	10,523	10,021	9,777	
V100	Pa s	2,232	1,943	1,910	1,608	
V500	Pa s	941	747	763	564	
Rheology ratio (V0.1/V100)	Ratio	3.9	5.4	5.2	6.1	
Mn SEC	kg/mol	42	32	33	28	
Mw SEC	kg/mol	112	113	113	112	
Mp - SEC	kg/mol	79	60	59	50	
Mz - SEC	kg/mol	222	259	263	277	
Mw/Mn – SEC	Ratio	2.7	3.5	3.5	4.0	
Mn TD	kg/mol	52	34	36	30	
Mw TD	kg/mol	132	130	126	119	
Mw/Mn TD	Ratio	2.5	3.8	3.6	3.9	
Mw TD / Mw SEC	Ratio	1.18	1.14	1.11	1.06	
g' avg	Ratio	0.85	0.89	0.89	0.91	

[0078] In addition to the ethylene-based polymers produced herein, two virgin ethylene-based polymers (CS-B and CS-C) and a PCR ethylene-based polymer (NATURA PCR-LDPCR-100) were used in the present examples.

[0079] CS-B refers to DOWLEX™ 2045G, a monomodal LLDPE produced in a single reactor, with a melt index (I₂) of 1 dg/min, and a density of 0.92 g/cc, commercially available from Dow Inc. Midland MI.

[0080] CS-C refers to a virgin bimodal ethylene-based polymer produced in a dual reactor, with a melt index (I₂) of 0.85 dg/min, and a density of 0.918 g/cc, commercially available from Dow Inc. Midland MI.

[0081] AVANGARD™ NATURA PCR-LDPCR-100, a PCR commercially available from Avangard Innovative LP, Houston, Texas (hereinafter “PCR”), is a post-consumer recycled ethylene-based polymer with a melt index (I₂) of 2 dg/min and a density of 0.914 g/cc.

Polymer Blend Production, Blown Film Fabrication, and Testing:

[0082] Polymer blends were formed by mixing the virgin ethylene-based polymers described herein with PCR ethylene-based polymers in an extruder. The properties of the polymer blends are described in Table 4.

[0083] Monolayer blown films were then fabricated having a target thickness of 2.0 mils were produced using a 2” die diameter blown film line. Gravimetric feeders dosed resin formulations into a Labtech LTE20-32 twin screw extruder at rate of 15 lbs/hr. From the extruder the resin formulation is conveyed into the 2” die diameter die with gap of 1.0mm. The LTE feed throat was set to 193 °C and the remaining barrel, conveying portion, and die temperature were set and maintained to 215 °C. To produce films an output rate of 2.4 lb/hr/in. of die circumference was targeted with pressurized ambient air inflating the film bubble to a 2.5 blow-up ratio. A dual lip air ring driven by a variable speed blower is used for all experiments. The frost line height (FLH) was maintained between 8.9 and 10.6 inches. Film thickness was targeted at 2 mils and was controlled within ± 10% by adjusting the nip roller speed. The films are wound up into a roll. Prior to testing the samples are conditioned for a minimum of 40hrs at 23 (+/- 2) °C and 50 (+/-10) % R.H. per ASTM D618 (Procedure A).

[0084] The produced films were then subjected to instrumented dart impact (IDI) testing, as described in the Test Methods.

Table 4

Sample	Base Sample MI (I ₂)	Base Sample Density	IDI (Joules)			
	(dg/min)	(g/cm ³)	0 wt. % PCR	20 wt. % PCR	40 wt. % PCR	70 wt. % PCR

S-1	0.76	0.916	13.6	2.92	1.50	0.43
S-2	0.79	0.917	12.1	2.95	1.55	0.37
S-3	0.93	0.918	10.2	2.82	1.46	0.45
CS-A	0.78	0.918	6.19	2.35	0.82	0.48
CS-B	1	0.92	0.43	0.31	0.33	0.34
CS-C	0.85	0.918	3.4	1.28	0.91	0.33

[0085] As can be seen in Table 4, the samples including the trimodal ethylene-based polymers S-1 to S-3 provided a higher IDI at a given PCR content than the comparative examples CS-A to CS-C.

[0086] 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 polymer blend comprising:
post-consumer recycled (PCR) ethylene-based polymer; and
trimodal ethylene-based polymer comprising first, second, and third polymer fractions
wherein 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.
2. The polymer blend of claim 1, wherein the trimodal ethylene-based polymer comprises a
density of 0.910 to 0.930 g/cc and a melt index (I₂) of 0.3 to 2 dg/min as measured according to
ASTM D1238 (190 °C, 2.16 Kg).
3. The polymer blend of claims 1 or 2, wherein the trimodal ethylene-based polymer comprises a
melt index (I₂) of 0.5 to 1 dg/min as measured according to ASTM D1238 (190 °C, 2.16 Kg).
4. The polymer blend of any one of claims 1 to 3, wherein the PCR ethylene-based polymer has
a density of 0.900 to 0.930 g/cc and a melt index (I₂) of 0.5 to 3 dg/min.
5. The polymer blend of any one of claims 1 to 4, wherein the polymer blend comprises 20 to 50
wt.% of the PCR ethylene-based polymer.
6. The polymer blend of claim 1 or 5, wherein the polyene comprises acyclic unconjugated
dienes.
7. The polymer blend of any one of claims 1 to 6, wherein the polyene comonomer comprises
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.
8. The polymer blend of any one of claims 1 to 7, wherein the first fraction has a density of less
than 0.925 g/cc, a melt index (I₂) less than 0.5 dg/min, and an MWD less than 3.0.

9. The polymer blend of any one of claims 1 to 8, wherein at least one of the first, second, and third polymer fractions are substantially free of long chain branching.
10. The polymer blend of any one of claims 1 to 9, wherein the trimodal ethylene-based polymer comprises from 45 to 65 wt.% first fraction and 35 to 55 wt.% of the sum of the second and third polymer fractions.
11. A film comprising the polymer blend any one of claims 1 to 10.
12. The film of claim 11, wherein the film is a monolayer or multilayer film.
13. The film of claim 11 or 12, wherein the film has an average thickness of 1-3 mil.
14. The film of claim 13, wherein the film has an instrumented dart impact (IDI) of at least 0.5 J, or preferably at least 2 J.