

POLYMER BLENDS INCLUDING POST-CONSUMER RECYCLED (PCR) ETHYLENE-BASED POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/579,102 filed August 28, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

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

BACKGROUND

[0003] PCR films have inferior optical properties compared to most virgin polyethylene films due to contamination and excessive thermal history associated with the recycling process. These inferior optical properties are believed to be caused by the increased prevalence of foreign contamination and/or polymer degradation (measured as the defect count) in typical PCR films, relative to typical virgin polyethylene films. These inferior properties make it challenging to incorporate PCR polymers into high end film applications at meaningful concentrations of PCR for improved sustainability.

[0004] Accordingly, there is a need for films which meet the optical standards while still incorporating meaningful amounts of PCR.

BRIEF SUMMARY

[0005] Embodiments of the present disclosure meet this need by providing films comprising a blend of PCR ethylene-based polymer and virgin ethylene-based polymer comprising polyene comonomer. Without being limited by theory, the polyene comonomer facilitates long chain branching and thereby increased melt strength (e.g., melt strength greater than 9 cN) in the virgin ethylene-based polymer. This increased melt strength was surprisingly found to reduce defect count when the polymer blend is formed.

[0006] According to one or more embodiments, a polymer blend may comprise: virgin ethylene-based polymer comprising the polymerized reaction product of ethylene monomer, C₃-C₁₄ alpha-olefin comonomer, and polyene comonomer, wherein the virgin-ethylene-based polymer comprises a melt strength (MS) greater than 9 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); and post-consumer recycled (PCR) ethylene-based polymer.

[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 to polymer blends comprising post-consumer recycled (PCR) ethylene-based polymer; and virgin 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 virgin ethylene-based polymer, on the basis of the total weight of the polymer blend.

[0023] The polymer blend may comprise 10 to 90 wt.% of the PCR ethylene-based polymer. In embodiments, the polymer blend may comprise from 10 to 85 wt. %, from 10 to 80 wt. %, from 20 to 90 wt. %, from 30 to 90 wt. %, from 40 to 90 wt. %, from 50 to 90 wt. %, from 60 to 90 wt. %, from 70 to 90 wt. %, from 35 to 85 wt. %, from 40 to 80 wt. %, from 30 to 50 wt. %, or any subset thereof, of the PCR ethylene-based polymer, on the basis of the total weight of the polymer blend.

Virgin Ethylene-Based Polymer

[0024] The virgin ethylene-based polymer comprises the polymerized reaction product of ethylene monomer, C₃-C₁₄ alpha-olefin comonomer, and polyene comonomer.

[0025] The virgin ethylene-based polymer may be unimodal or multimodal. In embodiments, the virgin ethylene-based polymer may be unimodal, bimodal, or trimodal.

[0026] The polyene comonomer may comprise acyclic unconjugated dienes. In embodiments, 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. The C₃-C₁₄ alpha-olefin comonomer may include one or more of 1-propylene, 1-butene, 1-hexene, 1-octene, or combinations thereof.

[0027] The virgin ethylene-based polymer may have a melt index (I₂) of 0.3 to 3 dg/min, such as 0.3 to 2 dg/min, 0.3 to 1 dg/min, 0.5 to 3 dg/min, 1 to 3 dg/min, 2 to 3 dg/min, 1 to 2 dg/min or any subset thereof, as measured according to ASTM D1238 (190 °C, 2.16 Kg).

[0028] The virgin ethylene-based polymer may have 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.

[0029] The virgin ethylene-based polymer may have an average g' greater than 0.860, greater than 0.880, or greater than 0.900, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector.

[0030] As noted above, the virgin ethylene-based polymer has excellent processibility, which can be quantified in part by its melt strength. As further noted above, the reduced defect count when the blend is incorporated into a film is attributed to the higher melt strength (e.g., melt strength > 9 cN) in the virgin ethylene-based polymer. In one or more embodiments, the virgin ethylene-based polymer may have a melt strength (MS) of at least 9 cN wherein MS is the melt strength in cN (Rheotens device, 190°C , 2.4 mm/s^2 , 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) of the virgin ethylene-based polymer is at least 10 cN, at least 12 cN, at least 13 cN, at least 20 cN, from 9 cN to 35 cN, from 10 to 35 cN, from 12 cN to 35 cN, from 20 cN to 35 cN, or any subset thereof.

[0031] Methods (including monomers, catalysts, and reactor types) of producing virgin ethylene-based polymers suitable for use in the present polymer blends are disclosed in, for example, U.S. Patent Applications U.S. 2022/0033547, U.S. 2022/0227905, and U.S. 2023/0128663; and U.S. Provisional Patent Application U.S. 63/510,769, the entirety of which are incorporated by reference herein.

[0032] The unimodal virgin resins ethylene-based polymers suitable for use in the present polymer blends may be produced by a dual chain catalyst as described in U.S. Patent Applications U.S. 2022/0033547, which is incorporated herein in its entirety. The multimodal virgin resins (e.g., bimodal and trimodal) may be produced by at least one dual chain catalyst, and at least one single chain catalyst.

[0033] In one or more embodiments, the single-chain catalyst may include, but is not limited to, a Ziegler-Natta catalyst, a chromium catalyst, a metallocene catalyst, a post-metallocene catalyst, a constrained geometry complex (CGC) catalyst, a phosphinimine catalyst, or a bis(phenylphenoxy) catalyst. Details and examples of CGC catalysts are provided in U.S. Pat. Nos. 5,272,236; 5,278,272; 6,812,289; and WO Publication 93/08221, which are all incorporated herein by reference in their entirety. Details and examples of bis(phenylphenoxy) catalysts are provided in U.S. Pat. Nos. 6,869,904; 7,030,256; 8,101,696; 8,058,373; 9,029,487, which are all incorporated herein by reference in their entirety.

PCR Ethylene-Based Polymer

[0034] 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.

[0035] 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.

[0036] 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.

[0037] The PCR ethylene-based polymer may have a melt index (I_2) of 0.3 to 3 dg/min. In embodiments, the PCR ethylene-based polymer may have a melt index (I_2) of 0.3 to 2.5 dg/min, 0.3 to 2.0 dg/min, 0.3 to 1.5 dg/min, 0.3 to 1.0 dg/min, 0.5 to 3 dg/min, 1 to 3 dg/min, 1.5 to 3 dg/min, 2 to 3 dg/min, 1 to 2.5 dg/min, 1.5 to 2.5 dg/min, or any subset thereof.

[0038] When fabricated into a film, the PCR ethylene-based polymer may have a GI400 defect count of at least 10 mm² defect area per 24.6 cm³ film volume, such as at least 25 mm² defect area per 24.6 cm³ film volume, at least 50 mm² defect area per 24.6 cm³ film volume, at least 100 mm² defect area per 24.6 cm³ film volume, at least 250 mm² defect area per 24.6 cm³ film volume, at least 500 mm² defect area per 24.6 cm³ film volume, at least 1000 mm² defect area per 24.6 cm³ film volume, at least 1500 mm² defect area per 24.6 cm³ film volume, at least 2000 mm² defect area per 24.6 cm³ film volume, at least 2500 mm² defect area per 24.6 cm³ film volume, from 10 mm² defect area per 24.6 cm³ film volume to 5000 mm² defect area per 24.6 cm³ film volume, from 10 mm² defect area per 24.6 cm³ film volume to 10,000 mm² defect area per 24.6 cm³ film volume, or any subset thereof.

[0039] Suitable PCR ethylene-based polymers include AVANGARD™ NATURA PCR-LDPCR-100 ("AVANGARD™ 100") and AVANGARD™ NATURA PCR-LDPCR-150

(“AVANGARD™ 150”) (PCR commercially available from Avangard Innovative LP, Houston, Texas).

Films

[0040] Additional embodiments of the present disclosure are directed to films. The films may include the polymer blends described herein. In embodiments, the films may comprise at least 80 wt. %, at least 90 wt. %, at least 95 wt. %, or at least 99 wt. % of the polymer blends described herein. In embodiments, the film is substantially free of any other polymeric component.

[0041] The film of may be a monolayer or multilayer film, such as a film having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11 layers. 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.

[0042] The film may have a defect count of less than 2000 as measured according to GI400 (mm² defect area per 24.6 cm³ film volume). In embodiments, the film may have a defect count of less than 1950, less than 1900, less than 1800, less than 1600, less than 1400, less than 1200, less than 1000, less than 950, less than 900, less than 800, less than 700, less than 600, less than 500, less than 400, less than 300, less than 200, less than 100, or even less than 50. In embodiments, the film may have the defect count of less than 2000 when the polymer blend comprises at least 40 wt. % of PCR ethylene based polymer, such as at least 80 wt. % of PCR ethylene based polymer.

[0043] 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

[0044] It should be understood that the above-described PCR ethylene-based polymers, the virgin 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. In embodiments, the polymer blend may comprise from 0 to 40 wt. %, such as from 0 to 30 wt. %, from 0 to 20 wt. %, from 0 to 10 wt. %, from 1 to 40 wt. %, from 1 to 30 wt. %, from 1 to 20 wt. %, or from 1 to 10 wt. % of additives.

Articles

[0045] 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

GI400 Polymer Defect Count

[0046] GI400 polymer defect count is a measure of defects that are detected in an extruded film using optical imaging technology in accordance with ASTM D7310-20 “Standard Practice for Defect Detection and Rating of Plastic Film Using Optical Sensors.” The Defect Count is reported as the area of optical defects (in mm²) per 24.6 cm³ film with an effective circular diameter within defined series of ranges: 400-800μm, 800-1600μm, 1600μm and above. It is measured by an Optical Control Systems Film Surface Analyzer FSA100 (OCS FSA100) optical imaging system. The OCS FSA100 optical imaging system consists of a lighting unit, a CCD line scan camera, and a computer with image/data analysis software version 10.4.1.7.

[0047] The OCS FSA100 optical imaging system detects defects as they obscure the transmission of halogen-based source light. Average greyscale was set to 170 with a threshold sensitivity setting of 35%. Additionally, the gain of the CCD system may be adjusted to compensate for film haziness. The imaging system creates a composite area of each defect by adding the defective pixels from each subsequent line scan. The system then reports the

area of defects which were in user defined size ranges, based on the diameter of circles having equivalent areas.

Film Fabrication

[0048] Blown films 2 mil thick were produced for Defect Counts as follows. Gravimetric feeders dosed resin formulations into a Labtech LTE20-32 twin screw extruder at rate of 15 lbs/hr. From the extruder the resin formulation is conveyed into the 2" die diameter die with gap of 1.0 mm. The LTE feed throat was set to 193°C and the remaining barrel, conveying portion, and die temperature were set and maintained to 215°C. Pressurized ambient air inflated the film bubble to a 2.5 blow-up ratio. A dual lip air ring driven by a variable speed blower is used for all experiments. The frost line height (FLH) was maintained between 8.8 and 10.8 inches. Film thickness was targeted at 2 mils and was controlled within $\pm 15\%$ by adjusting the nip roller speed. The films are wound up into a roll.

Melt Index

[0049] 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.

Density

[0050] 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.

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

[0051] The GPC-SEC (Conventional GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

Triple Detector GPC (TD) (Absolute GPC)

[0052] The GPC-TD (Absolute GPC) measurements were performed according to the test procedure defined in PCT Publication WO2021195502A1.

Dynamic Mechanical Spectroscopy (DMS)

[0053] The DMS measurements were performed according to the test procedure defined in PCT Publication WO2019067239A1.

Melt Strength (MS)

[0054] The DMS measurements were performed according to the test procedure defined in PCT Publication WO2019067239A1.

EXAMPLES

[0055] 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:

[0056] A series of virgin ethylene-based polymers were prepared as follows:

[0057] Bimodal ethylene-based polymers S-2 to S-6 were produced in single reactors with a multi-chain catalyst and a single-chain catalyst therein. Trimodal ethylene-based polymer S-1 was produced in a dual reactor having a multi-chain catalyst and two single-chain catalysts therein. Comparative Examples CS-A to CS-C were trimodal ethylene-based polymer produced in a dual reactor system having a multi-chain catalyst and two single-chain catalysts. Comparative Example CS-D was a bimodal ethylene-based polymer produced in a dual reactor system having two single-chain catalysts. Comparative Example CS-E was a bimodal ethylene-based polymer produced in a single reactor system having a single-chain catalyst and a multi-chain catalyst.

[0058] 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.

[0059] Two different reactor configurations were used: a single reactor system and a dual reactor system in a parallel mode. 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 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.

[0060] 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. In both single and dual reactor configurations, 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).

[0061] 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 polymer melt was pelletized and collected. There was no recycle in this process, but in general recycle can be achieved.

Table 1A: Dual Reactor Polymers

Example		S-1	CS-A	CS-B	CS-C	CS-D
Reactor Configuration	Type	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel	Dual Parallel
Comonomer type	Type	Octene	Octene	Octene	Octene	Octene
Low Density Reactor (Rx1)						
Rx1 Feed Solvent / Ethylene Mass Flow Ratio	g/g	8.4	8.5	8.4	8.4	8.5
Rx1 Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.08	0.06	0.06	0.06	0.08
Rx1 Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.2E-04	1.1E-04	1.1E-04	1.1E-04	1.2E-04
Rx1 Temperature	°C	160	160	160	160	160
Rx1 Pressure	Barg	28	28	28	28	28
Rx1 Ethylene Conversion	%	83.2	82.9	83.1	83.2	82.9
Rx1 Catalyst-A Type	Type	Cat A	Cat A	Cat A	Cat A	Cat A
Rx1 Co-Catalyst I Type	Type	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
Rx1 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.4	1.3	1.3	1.2	1.0
Rx1 Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	64.5	37.7	35.7	36.5	54.6
Rx1 [Al] from Co-Catalyst 2	Ppmw	0.93	0.76	0.76	0.76	0.93
Rx1 Residence Time	Min	8.3	6.8	6.8	6.8	8.3
Percentage of Total Ethylene Feed to Rx1	wt. %	52.5%	57.3%	57.3%	57.3%	52.3%
Rx1 Production Split	wt. %	53.3	59.4	59.8	59.8	54.8
High Density Reactor (Rx2)						
Rx2 Feed Solvent / Ethylene Mass Flow Ratio	g/g	7.5	7.5	7.5	7.5	7.5
Rx2 Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.274	0.166	0.135	0.135	0.124
Rx2 Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.3E-04	1.1E-04	1.1E-04	1.4E-04	8.4E-05
Rx2 Feed Ethylene/Pentadiene Mass Flow Ratio	g/g	2095	1369	2116	2104	
Rx2 Temperature	°C	150	150	150	150	150
Rx2 Pressure	Barg	28	28	28	28	28
Rx2 Ethylene Conversion	%	90.2	90.2	90.3	90.3	90.3
Rx2 Catalyst 1 Type	Type	Cat B	Cat B	Cat B	Cat B	Cat B
Rx2 Catalyst 2 Type	Type	Cat C	Cat C	Cat C	Cat C	None
Rx2 Co-Catalyst 1 Type	Type	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
Rx2 Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.2	1.2	1.2	1.2	1.2
Rx2 Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	5.9	12.9	11.4	8.3	40.7
Rx2 Residence Time	Min	12.6	12.6	12.7	12.6	12.7
Rx2 Production Split	wt. %	46.7	40.6	40.2	40.2	45.2

Table 1B: Single Reactor Polymers

		S-2	S-3	S-4	S-5	S-6	CS-E
Single Reactor							
Feed Solvent / Ethylene Mass Flow Ratio	g/g	7.03	6.99	7.00	6.03	6.02	7.11

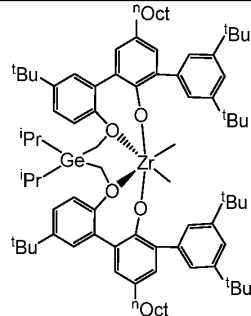
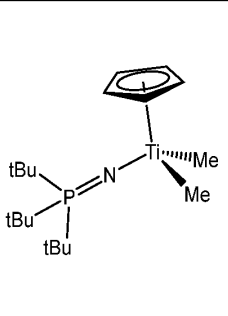
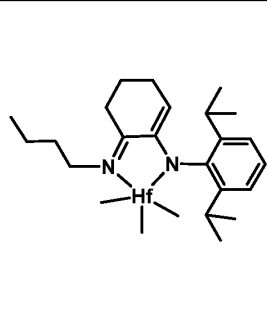
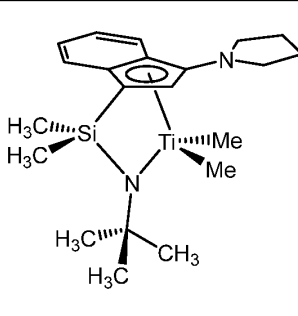
Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.53	0.53	0.48	0.35	0.28	0.41
Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	3.98 E-05	3.98 E-05	2.95 E-05	1.35 E-03	2.50 E-04	2.02 E-05
Feed Ethylene/Pentadiene Mass Flow Ratio	g/g	587	1177	1178	252	717	1940
Temperature	°C	150.7	152.8	150.0	140.0	140.0	150.0
Pressure	Barg	28.0	28.0	28.0	28.0	30.66	28.0
Ethylene Conversion	%	90.3	90.3	90.7	90.3	90.6	90.7
Catalyst 1 Type	Type	Cat B	Cat B	Cat B	Cat C	Cat D	Cat B
Catalyst 2 Type	Type	Cat C	Cat C	Cat C	None	Cat C	Cat C
Co-Catalyst 1 Type	Type	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A	CoCat A
Co-Catalyst 2 Type	Type	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B	CoCat B
Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	32.6	14.9	12.3	1.2	3.8	1.2
Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	103.3	74.3	77.6	3.1	6.3	7.6
Residence Time	Min	8.4	8.4	8.5	8.2	8.1	8.5

[0062] Co-catalyst A (CoCat A is bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate

[0063] Co-catalyst B (CoCat B) is MMAO-3A or modified methyl aluminoxane

[0064] The structures for Cat A, Cat B, Cat C, and Cat D which are noted in Tables 1A and 1B, are provided in Table 2 as follows.

Table 2

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

[0065] Details of the polymers produced are described in Table 3.

Table 3A

Example		S-2	S-3	S-4	S-5	S-6	CS-E
Polymer and Film Properties							
I ₂	dg/min	2.03	0.90	0.94	0.46	2.32	0.95
I ₁₀	dg/min	14.50	8.98	7.33	10.72	21.60	6.23
I ₁₀ /I ₂	Ratio	7.1	10.0	7.8	23.2	9.3	6.6
Density	g/cm ³	0.918	0.917	0.917	0.921	0.921	0.919
Melt strength	cN	30.9	22.3	13.0	9.1	24.0	5.2
Extensibility	mm/s	116	120	130	56	96	98
V _{0.01}	Pa s	7,141	33,805	15,486			
V _{0.1}	Pa s	4,253	13,588	9,939	30,028	5,610	
V ₁₀₀	Pa s	1,053	1,214	1,738	648	684	
V ₅₀₀	Pa s	602	647	840			
Rheology ratio (V _{0.1} /V ₁₀₀)	Ratio	4.0	11.2	5.7	46.3	8.2	
Mn SEC	kg/mol	34.3	35.2	41.3	13.4	21.1	46.4
Mw SEC	kg/mol	90.6	113.1	111.4	66.8	93.8	110.2
Mp - SEC	kg/mol	59.5	58.8	68.9	84.8	49.7	79.4
Mz - SEC	kg/mol	305.1	402.4	315.5	160.4	534.4	238.2
Mw/Mn - SEC	Ratio	2.6	3.2	2.7	5.0	4.4	2.7
Mn TD	kg/mol	35.8	41.2	47.5	15.7	20.5	47.8
Mw TD	kg/mol	105.5	134.9	127.0	85.2	104.1	109.1
Mw/Mn TD	Ratio	2.9	3.3	2.7	5.4	5.1	2.3
Mw TD / Mw SEC	Ratio	1.16	1.19	1.14	1.28	1.11	0.99
g' avg	Ratio	0.89	0.83	0.86	0.68	0.92	0.99

Table 3B

Example		S-1	CS-A	CS-B	CS-C	CS-D	CS-G
Polymer and Film Properties							
I ₂	dg/min	0.82	0.76	0.78	0.84	0.77	0.85
I ₁₀	dg/min	6.72	5.53	5.65	6.22	5.04	
I ₁₀ /I ₂	Ratio	8.2	7.3	7.2	7.4	6.5	
Density	g/cm ³	0.916	0.916	0.918	0.918	0.916	0.918
Melt strength	cN	13.3	5.3	4.6	4.7	3.2	4.4
Extensibility	mm/s	126	245	>250	>250	147	
V _{0.01}	Pa s	12,385	11,468	10,785	10,266	8,981	
V _{0.1}	Pa s	9,673	10,523	10,021	9,777	8,738	
V ₁₀₀	Pa s	1,551	1,943	1,910	1,608	2,232	
V ₅₀₀	Pa s	596	747	763	564	941	
Rheology ratio (V _{0.1} /V ₁₀₀)	Ratio	6.2	5.4	5.2	6.1	3.9	
Mn SEC	kg/mol	26	32	33	28	42	
Mw SEC	kg/mol	108	113	113	112	112	
Mp - SEC	kg/mol	42	60	59	50	79	

Example		S-1	CS-A	CS-B	CS-C	CS-D	CS-G
Mz - SEC	kg/mol	296	259	263	277	222	
Mw/Mn – SEC	Ratio	4.2	3.5	3.5	4.0	2.7	
Mn TD	kg/mol	25	34	36	30	52	
Mw TD	kg/mol	123	130	126	119	132	
Mw/Mn TD	Ratio	5.0	3.8	3.6	3.9	2.5	
Mw TD / Mw SEC	Ratio	1.14	1.14	1.11	1.06	1.18	
g' avg	Ratio	0.91	0.89	0.89	0.91	0.85	

[0066] CS-F 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.

[0067] CS-G 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.

[0068] 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. A film of 100 % PCR has a GI400 defect count of 2750 mm² defect area per 24.6 cm³ film volume, as determined by the measurement system and blown film process specified above.

Polymer Blend Production, Blown Film Fabrication, and Testing:

[0069] Polymer blends were formed by mixing the virgin ethylene-based polymers described herein with PCR ethylene-based polymers in an extruder. Properties of the polymer blends are described in Table 4.

[0070] The polymer blends were then fabricated into monolayer blown films having a target thickness of 2.0 mils and 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 $\pm 10\%$ 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).

[0071] The produced films were then subjected to polymer defect count testing, as described in the Test Methods. The results are given in Table 4.

Table 4

Virgin resin	MS of virgin resin (cN)	GI400 at 40% PCR (mm ² defect area per 24.6 cm ³ film volume)	GI400 at 80% PCR (mm ² defect area per 24.6 cm ³ film volume)
S-1	13.3	889	1830
S-2	30.9	10.3	590
S-3	22.3	49.5	1220
S-4	13.0	749	1920
S-5	9.1	153	1680
S-6	24.0	21.7	793
CS-A	5.3	1310	2430
CS-B	4.6	1350	2390
CS-C	4.7	1400	2500
CS-D	3.2	1190	2410
CS-E	5.2	998	2070
CS-F	3.2	1760	2530
CS-G	4.4	1400	2350

[0072] As can be seen in Table 4, the comparative samples CS-A to CS-G had a substantially greater GI400 defect count, at both 40 % and 80 % PCR, than did samples S-1 to S-6, which had a melt strength greater than 9 cN.

CLAIMS

1. A polymer blend comprising:

virgin ethylene-based polymer comprising the polymerized reaction product of ethylene monomer, C₃-C₁₄ alpha-olefin comonomer, and polyene comonomer, wherein the virgin-ethylene-based polymer comprises a melt strength (MS) greater than 9 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); and

post-consumer recycled (PCR) ethylene-based polymer.

2. The polymer blend of claim 1, wherein the PCR ethylene-based polymer has a density of 0.900 to 0.930 g/cc and a melt index (I₂) of 0.3 to 3 dg/min.

3. The polymer blend of claim 1 or 2 wherein the virgin ethylene-based polymer has a density of 0.910 to 0.930 g/cc and a melt index (I₂) of 0.3 to 3 dg/min as measured according to ASTM D1238 (190C, 2.16 Kg).

4. The polymer blend of claim 1 or 3 wherein the MS of the virgin ethylene-based polymer is at least 9 cN.

5. The polymer blend of any one of claims 1 to 4 wherein the polyene comprise acyclic unconjugated dienes.

6. The polymer blend of any one of claims 1 to 5 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.

7. The polymer blend of any one of claims 1 to 6, wherein the polymer blend comprises 10 to 90 wt.% of the PCR ethylene-based polymer.

8. The polymer blend of any one of claims 1 to 7, wherein the virgin ethylene-based polymer is unimodal or multimodal.

9. A film comprising the polymer blend any one of claims 1 to 8.

10. The film of claim 9, wherein the film is a monolayer or multilayer film.
11. The film of claim 9 or 10, wherein the film has an average thickness of 1-3 mil.
12. The film of any one of claims 9 to 11, wherein the film has a defect count of less than 1000 as measured according to GI400 (mm² defect area per 24.6 cm³ film volume).