POLYMER BLENDS INCLUDING RECYCLED ETHYLENE-BASED POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[1] This application claims the benefit of U.S. Provisional Application Serial No. 63/567,542 filed March 20, 2024, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[2] Embodiments are generally related to polymer blends; and more specifically are related to polymer blends that include virgin ethylene-based polymers and recycled ethylene-based polymers.

BACKGROUND

[3] Films that contain or partially contain post-consumer recycled (PCR) and/or post-industrial recycled (PIR) plastic have inferior physical properties compared to most virgin polyethylene films due to contamination and excessive thermal history associated with the recycling process. These inferior physical 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 and/or PIR films, relative to typical virgin polyethylene films. These inferior properties make it challenging to incorporate PCR and/or PIR polymers into high end film applications at meaningful concentrations of PCR and/or PIR for improved sustainability.

BRIEF SUMMARY

[4] Accordingly, there is an ongoing need to create films that incorporate recycled polyethylene while maintaining physical properties (e.g., instrumented dart impact (IDI)) comparable to virgin films.

[5] Embodiments of the present disclosure meet this need by providing films comprising recycled ethylene-based polymer and the virgin ethylene-based polymer as described below.

[6] According to one embodiments, the polymer blend includes virgin multimodal ethylene-based copolymer and recycled ethylene-based polymer. The virgin multimodal ethylene-based copolymer is the polymerized reaction product of ethylene and one or more

C_3-C_{14} olefinic comonomers, wherein the virgin multimodal ethylene-based copolymer comprises: a melt index (I_2) of from 0.5 g/10 minutes (g/10 min) to 10.0 g/10 min, when measured according to ASTM D-1238 at 190 °C and 2.16 kg; a melt strength (MS) $\geq 3.9/I_2 + 1.4$, 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 a light scattering cumulative detector fraction (CDF_{LS}) from 8% to 50%, wherein the CDF_{LS} is computed by measuring the area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using Gel Permeation Chromatography (GPC). The recycled ethylene-based polymer comprises post consumer recycled (PCR) ethylene-based polymer, post-industrial recycled (PIR) or combinations of PCR and PIR.

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

DETAILED DESCRIPTION

[8] Definitions

[9] 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.

[10] "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).

[11] 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/cm^3 to 0.930 g/cm^3.

[12] 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.

[13] "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.

[14] "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).

[15] 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.

[16] 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.

[17] 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.

[18] 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 and ESTL ultimate stretch.

[19] The term "pre-consumer recycled polyethylene" and refer to polymers, including blends of polyethylene polymers, recovered from pre-consumer material, as defined by ISO-14021. The generic term pre-consumer recycled polyethylene thus includes blends of polyethylene and other polymers recovered from materials diverted from the waste stream

during a manufacturing process. The generic term pre-consumer recycled polyethylene excludes the reutilization of polyethylene materials, such as rework, regrind, or scrap, generated in a process and capable of being reclaimed within the same process that generated it. In some instances, pre-consumer recycled polyethylene may include post-industrial recycled polyethylene.

[20] The term "post-consumer recycled" (or "PCR") polyethylene, as used herein, refers to a polyethylene material, such as the PCR HDPE, that includes materials previously used in a consumer or industry application i.e., pre-consumer recycled polyethylene and post-industrial recycled HDPE. PCR polyethylene is typically collected from recycling programs and recycling plants. The PCR polyethylene may include one or more contaminants. The contaminants may be the result of the polyethylene 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 polyethylene is distinct from virgin polyethylene. A virgin polyethylene does not include materials previously used in a consumer or industry application, whereas the PCR polyethylene does include them. Virgin polyethylene 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 polyethylene polymers differ when compared to virgin polyethylene, which in turn can present challenges to incorporating PCR polyethylene into blends for commercial use.

[21] It is contemplated that the PCR polyethylene includes various polyethylene compositions. PCR polyethylene may be sourced from HDPE packaging such as bottles (milk jugs, juice containers), LDPE/LLDPE packaging such as films. PCR polyethylene also includes residue from its original use, residue such as paper, adhesive, ink, nylon, ethylene vinyl alcohol (EVOH), polyethylene terephthalate (PET), and other odor-causing agents. Sources of PCR polyethylene can include, for example, bottle caps and closures, milk, water or orange juice containers, detergent bottles, office automation equipment (printers, computers, copiers, etc.), white goods (refrigerators, washing machines, etc.), consumer electronics (televisions, video cassette recorders, stereos, etc.), automotive shredder residue (the mixed materials remaining after most of the metals have been sorted from shredded automobiles and other metal-rich products "shredded" by metal recyclers), packaging waste,

household waste, rotomolded parts (kayaks/coolers), building waste and industrial molding and extrusion scrap.

[22] In embodiments, the polyethylene of the PCR polyethylene comprises low density polyethylene, linear low density polyethylene, or a combination thereof. In embodiments, the PCR polyethylene further comprises residue from its original use, such as paper, adhesive, ink, nylon, ethylene vinyl alcohol (EVOH), polyamide (PA), polyethylene terephthalate (PET), and other organic or inorganic material. Examples of PCR polymers include KWR101-150 and KWR-102 commercially available from KW Plastics, and AVANGARD™ NATURA PCR-LDPCR-100 ("AVANGARD™ 100") and AVANGARD™ NATURA PCR-LDPCR-150 ("AVANGARD™ 150") (PCR polymer commercially available from Avangard Innovative LP, Houston, Texas).

[23] "Recycled ethylene-based polymer" or "recycled polyethylene" encompasses embraces both pre-consumer recycled polymer and post-consumer recycled polymer. Recycled polymers are defined in ISO 14021 7.8.1.1.

[24] Polymer Blends

[25] Embodiments of the present disclosure are directed to polymer blends comprising recycled ethylene-based polymer; and virgin ethylene-based polymer. In embodiments, the polymer blend may comprise at least 80 wt. %, 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 recycled ethylene-based polymer and the virgin ethylene-based polymer, on the basis of the total weight of the polymer blend.

[26] The polymer blend may comprise 10 to 90 wt.% of the recycled 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 recycled ethylene-based polymer, on the basis of the total weight of the polymer blend.

[27] Virgin Ethylene-Based Polymer

[28] The virgin ethylene-based polymer comprises the polymerized reaction product of ethylene monomer, one or more C_3-C_{14} olefinic comonomer(s). The virgin ethylene-based

polymer may be multimodal. In one or more embodiments, the virgin ethylene-based polymer may be bimodal or trimodal.

[29] In embodiments, the one or more C_3-C_{14} olefinic comonomers may be an α-olefin co-monomers. In some embodiments, the C_3-C_{14} α-olefin comonomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary C_3-C_{14} α-olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-l-pentene. For example, the one or more α-olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

[30] In one or more embodiments, the virgin multimodal ethylene-based copolymer composition may have a density of 0.900 g/cm^3 to 0.940 g/cm^3. For example, embodiments of the presently-disclosed virgin multimodal ethylene-based copolymer composition may have densities of from 0.900 g/cm^3 to 0.925 g/cm^3, from 0.900 g/cm^3 to 0.920 g/cm^3, from 0.900 g/cm^3 to 0.918 g/cm^3, from 0.900 g/cm^3 to 0.916 g/cm^3, from 0.900 g/cm^3 to 0.914 g/cm^3, from 0.900 g/cm^3 to 0.912 g/cm^3, from 0.900 g/cm^3 to 0.910 g/cm^3, from 0.900 g/cm^3 to 0.908 g/cm^3, from 0.900 g/cm^3 to 0.906 g/cm^3, from 0.900 g/cm^3 to 0.904 g/cm^3, from 0.900 g/cm^3 to 0.902 g/cm^3, from 0.902 g/cm^3 to 0.920 g/cm^3, from 0.902 g/cm^3 to 0.918 g/cm^3, from 0.902 g/cm^3 to 0.916 g/cm^3, from 0.902 g/cm^3 to 0.914 g/cm^3, from 0.902 g/cm^3 to 0.912 g/cm^3, from 0.902 g/cm^3 to 0.910 g/cm^3, from 0.902 g/cm^3 to 0.908 g/cm^3, from 0.902 g/cm^3 to 0.906 g/cm^3, from 0.902 g/cm^3 to 0.904 g/cm^3, from 0.904 g/cm^3 to 0.920 g/cm^3, from 0.904 g/cm^3 to 0.918 g/cm^3, from 0.904 g/cm^3 to 0.916 g/cm^3, from 0.904 g/cm^3 to 0.914 g/cm^3, from 0.904 g/cm^3 to 0.912 g/cm^3, from 0.904 g/cm^3 to 0.910 g/cm^3, from 0.904 g/cm^3 to 0.908 g/cm^3, from 0.904 g/cm^3 to 0.906 g/cm^3, from 0.906 g/cm^3 to 0.920 g/cm^3, from 0.906 g/cm^3 to 0.918 g/cm^3, from 0.906 g/cm^3 to 0.916 g/cm^3, from 0.906 g/cm^3 to 0.914 g/cm^3, from 0.906 g/cm^3 to 0.912 g/cm^3, from 0.906 g/cm^3 to 0.910 g/cm^3, from 0.906 g/cm^3 to 0.908 g/cm^3, from 0.908 g/cm^3 to 0.920 g/cm^3, from 0.908 g/cm^3 to 0.918 g/cm^3, from 0.908 g/cm^3 to 0.916 g/cm^3, from 0.908 g/cm^3 to 0.914 g/cm^3, from 0.908 g/cm^3 to 0.912 g/cm^3, from 0.908 g/cm^3 to 0.910 g/cm^3, from 0.910 g/cm^3 to 0.920 g/cm^3, from 0.910 g/cm^3 to 0.918 g/cm^3, from 0.910 g/cm^3 to 0.916 g/cm^3, from 0.910 g/cm^3 to 0.914 g/cm^3, from 0.910 g/cm^3 to 0.912 g/cm^3, from 0.912 g/cm^3 to 0.920 g/cm^3, from 0.912 g/cm^3 to 0.918 g/cm^3, from 0.912 g/cm^3 to 0.916 g/cm^3, from 0.912 g/cm^3 to 0.914 g/cm^3, from 0.914 g/cm^3 to 0.920 g/cm^3, from 0.914 g/cm^3 to 0.918 g/cm^3, from 0.914 g/cm^3 to 0.916

g/cm^3, from 0.916 g/cm^3 to 0.920 g/cm^3, from 0.916 g/cm^3 to 0.918 g/cm^3, from 0.918 g/cm^3 to 0.920 g/cm^3, or any combination of these ranges.

[31] In one or more embodiments, the virgin multimodal ethylene-based copolymer composition may have a melt index (I_2) of from 0.50 g/10 minutes (g/10 min) to 10.0 g/10 min when measured according to ASTM D-1238 at 190 °C and 2.16 kg. In one or more embodiments, the virgin multimodal ethylene-based copolymer composition may have a melt index (I_2) of from 0.5 g/10 min to 10.0 g/10 min, from 0.5 g/10 min to 9.0 g/10 min, from 0.5 g/10 min to 8.0 g/10 min, from 0.5 g/10 min to 7.0 g/10 min, from 0.5 g/10 min to 6.0 g/10 min, from 0.5 g/10 min to 5.0 g/10 min, from 0.5 g/10 min to 4.0 g/10 min, from 0.5 g/10 min to 3.0 g/10 min, from 0.5 g/10 min to 2.0 g/10 min, from 0.5 g/10 min to 1.0 g/10 min, from 1.0 g/10 min to 10.0 g/10 min, from 1.0 g/10 min to 9.0 g/10 min, from 1.0 g/10 min to 8.0 g/10 min, from 1.0 g/10 min to 7.0 g/10 min, from 1.0 g/10 min to 6.0 g/10 min, from 1.0 g/10 min to 5.0 g/10 min, from 1.0 g/10 min to 4.0 g/10 min, from 1.0 g/10 min to 3.0 g/10 min, from 1.0 g/10 min to 2.0 g/10 min, from 2.0 g/10 min to 10.0 g/10 min, from 2.0 g/10 min to 9.0 g/10 min, from 2.0 g/10 min to 8.0 g/10 min, from 2.0 g/10 min to 7.0 g/10 min, from 2.0 g/10 min to 6.0 g/10 min, from 2.0 g/10 min to 5.0 g/10 min, from 2.0 g/10 min to 4.0 g/10 min, from 2.0 g/10 min to 3.0 g/10 min, from 3.0 g/10 min to 10.0 g/10 min, from 3.0 g/10 min to 9.0 g/10 min, from 3.0 g/10 min to 8.0 g/10 min, from 3.0 g/10 min to 7.0 g/10 min, from 3.0 g/10 min to 6.0 g/10 min, from 3.0 g/10 min to 5.0 g/10 min, from 3.0 g/10 min to 4.0 g/10 min, from 4.0 g/10 min to 10.0 g/10 min, from 4.0 g/10 min to 9.0 g/10 min, from 4.0 g/10 min to 8.0 g/10 min, from 4.0 g/10 min to 7.0 g/10 min, from 4.0 g/10 min to 6.0 g/10 min, from 4.0 g/10 min to 5.0 g/10 min, from 5.0 g/10 min to 10.0 g/10 min, from 5.0 g/10 min to 9.0 g/10 min, from 5.0 g/10 min to 8.0 g/10 min, from 5.0 g/10 min to 7.0 g/10 min, from 5.0 g/10 min to 6.0 g/10 min, from 6.0 g/10 min to 10.0 g/10 min, from 6.0 g/10 min to 9.0 g/10 min, from 6.0 g/10 min to 8.0 g/10 min, from 6.0 g/10 min to 7.0 g/10 min, from 7.0 g/10 min to 10.0 g/10 min, from 7.0 g/10 min to 9.0 g/10 min, from 7.0 g/10 min to 8.0 g/10 min, from 8.0 g/10 min to 10.0 g/10 min, from 8.0 g/10 min to 9.0 g/10 min, from 9.0 g/10 min to 10.0 g/10 min, or any combination of these ranges, when measured according to ASTM D-1238 at 190 °C and 2.16 kg.

[32] According to embodiments, the virgin multimodal ethylene-based copolymer composition may have a molecular weight distribution, expressed as the ratio of the weight average molecular weight to number average molecular weight (Mw/Mn), in the range of

from 2.0 to 6.0. For example, the virgin multimodal ethylene-based copolymer composition may have a molecular weight distribution of from 2.0 to 5.5, 2.0 to 5.0, 2.0 to 4.5, 2.0 to 4.0, 2.0 to 3.5, 2.0 to 3.0, 2.0 to 2.5, 2.5 to 6.0, 3.0 to 5.5, 3.0 to 5.0, 3.0 to 4.5, 3.0 to 4.0, 3.0 to 3.5, 3.5 to 6.0, 3.5 to 5.5, 3.5 to 5.0, 3.5 to 4.5, 3.5 to 4.0, 4.0 to 6.0, 4.0 to 5.5, 4.0 to 5.0, 4.0 to 4.5, 4.5 to 6.0, 4.5 to 5.5, 4.5 to 5.0, 5.0 to 6.0, 5.0 to 5.5, or 5.5 to 6.0, or any combination of these ranges. As presently described, the molecular weight distribution may be calculated according to gel permeation chromatography (GPC) techniques as described herein.

[33] The long chain branching frequency (LCB_f) refers to the level of long chain branches per 1000 carbons. In embodiments, the long chain branching frequency (LCB_f) of the virgin multimodal ethylene-based copolymer composition is greater than or equal to 0.3 and less than or equal to 1.0. In one or more embodiments, the long chain branching frequency (LCB_f) of the virgin multimodal ethylene-based copolymer composition may be from 0.3 to 1.0, from 0.3 to 0.8, from 0.3 to 0.7, from 0.3 to 0.6, from 0.5 to 1.0, from 0.5 to 0.9, from 0.5 to 0.8, from 0.8 to 1.0 or any combination of these ranges.

[34] According to embodiments, the virgin multimodal ethylene-based copolymer composition may have a melt strength (MS) defined by the following equation: $MS \geq 3.9/I_2 + 1.4$, wherein I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C. According to one or more embodiments, the virgin multimodal ethylene-based copolymer composition may have a melt strength of at least 5 centiNewtons (cN), or at least 8 cN. In further embodiments, the virgin multimodal ethylene-based copolymer composition may have a melt strength of from 5 cN to 50 cN, from 5 cN to 45 cN, from 5 cN to 40 cN, from 5 cN to 35 cN, from 5 cN to 30 cN, from 5 cN to 25 cN, from 5 cN to 20 cN, from 5 cN to 15 cN, from 5 cN to 10 cN, from 10 cN to 50 cN, from 10 cN to 45 cN, from 10 cN to 40 cN, from 10 cN to 35 cN, from 10 cN to 30 cN, from 10 cN to 25 cN, from 10 cN to 20 cN, from 10 cN to 15 cN, from 15 cN to 50 cN, from 15 cN to 45 cN, from 15 cN to 40 cN, from 15 cN to 35 cN, from 15 cN to 30 cN, from 15 cN to 25 cN, from 15 cN to 20 cN, from 20 cN to 50 cN, from 20 cN to 45 cN, from 20 cN to 40 cN, from 20 cN to 35 cN, from 20 cN to 30 cN, from 20 cN to 25 cN, from 25 cN to 50 cN, from 25 cN to 45 cN, from 25 cN to 40 cN, from 25 cN to 35 cN, from 25 cN to 30 cN, from 30 cN to 50 cN, from 30 cN to 45 cN, from 30 cN to 40 cN, from 30 cN to 35 cN, from 35 cN to 50 cN, from

35 cN to 45 cN, from 35 cN to 40 cN, from 40 cN to 50 cN, from 40 cN to 45 cN, or from 45 cN to 50 cN.

[35] In embodiments, the virgin multimodal ethylene-based copolymer composition may have a ratio of viscosity measured at 0.1 radians/second and 190 °C to viscosity measured at 100 radians/second and 190 °C (V0.1/V100), as determined by dynamic mechanical analysis, of greater than 5. In further embodiments, the virgin multimodal ethylene-based copolymer composition may have a (V0.1/V100), as determined by dynamic mechanical analysis, of from 5 to 30, from 5 to 25, from 5 to 20, from 5 to 15, from 5 to 10, from 10 to 30, from 10 to 25, from 10 to 20, from 10 to 15, from 15 to 30, from 15 to 25, from 15 to 20, from 20 to 30, from 20 to 25, or from 25 to 30.

[36] In embodiments, the cumulative distribution fractions (CDF) for light scattering analysis (CDF_{LS}) at a molecular weight greater than 500,000 g/mol is greater than or equal to 8%. In some embodiments, the cumulative distribution fractions (CDF) for light scattering analysis (CDF_{LS}) at a molecular weight greater than 500,000 g/mol is 8% to 50%.

[37] In embodiments, the virgin multimodal ethylene-based copolymer composition may have a high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, of from 8% to 50%. In embodiments, the high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, may be from 8% to 40%, from 8% to 30%, from 8% to 20% from 8% to 10%, from 10% to 50%, from 10% to 40%, from 10% to 30%, from 10% to 20%, from 20% to 50%, from 20% to 40%, from 20% to 30%, from 30% to 50%, from 30% to 40%, or from 40% to 50%. In embodiments, the virgin multimodal ethylene-based copolymer composition may have a low molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram less than 500,000 g/mol using GPC molecular weight distribution, of greater than 50%. In embodiments, the low molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram less than 500,000 g/mol using GPC molecular weight distribution, may be from 50% to 92%, from 50% to 90%, from 50% to 80% from 50% to 70%, from 50% to 60%, from 60% to 92%, from 60% to 90%, from 60% to 80%, from 60% to 70%, from 70% to 92%, from 70% to 90%, from 70% to 80%, from 80% to 92%, from

80% to 90%, or from 90% to 92%. Traditionally, it was thought that having as much high molecular weight material as possible was ideal because high molecular weight would lead to higher levels of entanglements that improve the properties of the LLDPE. Accordingly, low molecular weight material was kept to a minimum. However, the virgin multimodal ethylene-based copolymer compositions according to embodiments disclosed and described herein exhibit unique and unexpected characteristics compared to commercially available LDPE products when the high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, is from 8% to 50%.

[38] In embodiments, the amount of long-chain branching derived from the concentration of vinyl groups in the virgin multimodal ethylene-based copolymer composition produced expressed in vinyls/1,000 carbon atoms may be from 0.03 to 0.900 as derived from the concentration of vinyl groups in the produced expressed in vinyls/1,000 carbon atoms. Without being bound by theory, the vinyl end groups may enable the formation of long chain branching, which is a contributing factor to the melt strengths achieved in the virgin multimodal ethylene-based copolymer compositions described herein.

[39] The virgin multimodal ethylene-based copolymer compositions may further comprise one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, and combinations thereof. The virgin multimodal ethylene-based copolymer compositions may contain any amounts of additives. The virgin multimodal ethylene-based copolymer compositions may compromise from about 0 to about 10 percent by the combined weight of such additives, based on the total weight of the virgin multimodal ethylene-based copolymer compositions. The virgin multimodal ethylene-based copolymer compositions may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The virgin multimodal ethylene-based copolymer compositions may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $Mg(OH)_2$, based on the total weight of the virgin multimodal ethylene-based copolymer compositions. The virgin multimodal ethylene-based copolymer compositions may further be blended with one or more polymers to form a blend.

[40] Recycled Ethylene-Based Polymer

[41] The recycled 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 recycled ethylene-based polymer.

[42] The recycled ethylene-based polymer may comprise an LDPE, an HDPE, an LLDPE, or a blend thereof. In embodiments, the recycled 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 recycled ethylene-based polymer

[43] The recycled ethylene-based polymer may have a density of 0.900 to 0.930 g/cc. In embodiments, the recycled 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.

[44] The recycled ethylene-based polymer, for example, PCR may have a melt index (I_2) of 0.3 to 3 dg/min. In embodiments, the recycled 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.

[45] When fabricated into a film, the recycled ethylene-based polymer may have a defect count of at least 10 mm^2 defect area per 24.6 cm^3 film volume, such as at least 25 mm^2 defect area per 24.6 cm^3 film volume , at least 50 mm^2 defect area per 24.6 cm^3 film volume, at least 100 mm^2 defect area per 24.6 cm^3 film volume, at least 250 mm^2 defect area per 24.6 cm^3 film volume, at least 500 mm^2 defect area per 24.6 cm^3 film volume, at least 1000 mm^2 defect area per 24.6 cm^3 film volume, at least 1500 mm^2 defect area per 24.6 cm^3 film volume, at least 2000 mm^2 defect area per 24.6 cm^3 film volume, at least 2500 mm^2 defect area per 24.6 cm^3 film volume, from 10 mm^2 defect area per 24.6 cm^3 film volume to 5000 mm^2 defect area per 24.6 cm^3 film volume, from 10 mm^2 defect area per 24.6 cm^3 film volume to 10,000 mm^2 defect area per 24.6 cm^3 film volume, or any subset thereof.

[46] 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).

[47] Films

[48] 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.

[49] 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 properties of the film, the 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.

[50] The film may have a defect count of less than 2000 as measured according to GI400 (mm^2 defect area per 24.6 cm^3 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.

[51] 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.

[52] Additives

[53] 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.

[54] Articles

[55] 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

[56] Melt Index

[57] Melt indices I_2 and I_{10} of polymer samples, which have units of g/10 min or dg/min, were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively.

[58] Density

[59] 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.

[60] Triple Detection Gel Permeation Chromatography (GPC)

[61] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler

oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent "Mixed A" 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

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

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

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

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

[66] For the determination of the viscometer and light scattering detector offsets from the IR5 detector, the Systematic Approach for the determination of multi-detector offsets is done

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

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

[68] The absolute weight average molecular weight ($MW_{(Abs)}$) is obtained (using GPCOne™) from the Area of the Light Scattering (LS) integrated chromatogram (factored by the light scattering constant) divided by the mass recovered from the mass constant and the mass detector (IR5) area. The molecular weight and intrinsic viscosity responses are linearly extrapolated at chromatographic ends where signal to noise becomes low (using

GPCOne™). Other respective moments, $Mn_{(Abs)}$ and $Mz_{(Abs)}$ are be calculated according to equations 2-4 as follows :

[69] $$Mn(Abs) = \frac{\sum^i IR_i}{\sum^i (IR_i / M_{Absolute_i})} \quad \text{(EQ 2)}$$

[70] $$Mw(Abs) = \frac{\sum^i IR_i \times M_{Absolute_i}}{\sum^i IR_i} \quad \text{(EQ 3)}$$

[71] $$Mz(Abs) = \frac{\sum^i (IR_i \times M_{Absolute_i}{}^2)}{\sum^i (IR_i \times M_{Absolute_i})} \quad \text{(EQ 4)}$$

[72] Calculation of LCB frequency (LCB_f)

[73] The long chain branching frequency was calculated based on the differences between the g', which is a ratio of the intrinsic viscosity of a polymer sample over a linear polymer reference with the same molecular weight. In 3D GPC practice, a reference polyethylene homopolymer, containing no detectable LCB or SCB, and with a Mw of approximately 120,000 g/mol and polydispersity around 3.0, is injected at the beginning of each run queue to establish the Mark-Houwink linear reference line. A first-order linear fit is applied to the obtained log of the intrinsic viscosity and log of the molecular weight data within the log of the molecular weight range of 4.5 to 5.8 g/mol to provide the linear reference K and α values.

[74] A polyethylene sample of interest is analyzed to obtain intrinsic viscosity, molecular weight values, and the value of g_i' is calculated at each chromatographic slice (i) according to Equation 5:

[75] $g_i' = (IV_{Sample,i} / IV_{linear\ reference,i})$ (Eq. 5),

[76] where the calculation utilizes the $IV_{Sample,i}$ at equivalent absolute molecular weight values and same SCB content values to the linear reference within the log molecular weight range of 4.5 to 5.8 g/mol. If a difference in SCB content exists, the $IV_{linear\ reference,i}$ line is vertically shifted by adjusting the K value from the Mark-Houwink Plot to account for the SCB correction compared to the $IV_{Sample,i}$. The shift is done until the linear reference line makes a single point of contact to make a tangent with the sample Mark-Houwink line at a log molecular weight of 4.5.

[77] A Zimm-Stockmayer branching factor g was calculated from g', $g' = g^{\varepsilon}$, using an epsilon factor of 0.5. The number of branches along the polymer sample (B_n) at each data slice (i) can be determined by using Equation 6, (B. H. Zimm and W. H. Stockmayer, J. Chem. Phys. **17**, 1301 (1949)):

[78] $$g = \left[\left(1 + \frac{B_{n,i}}{7} \right)^{1/2} + \frac{4}{9} \frac{B_{n,i}}{\pi} \right]^{-1/2} \quad \text{(Eq. 6).}$$

[79] Finally, the average LCBf quantity per 1000 carbons in the polymer across all of the slices (i) can be determined using Equation 7:

[80] $$LCBf = \frac{\sum^{i} \left(\frac{B_{n,i}}{M_i / 14000} c_i \right)}{\sum c_i} \quad \text{(Eq. 7).}$$

[81] CDF Calculation Method

[82] Calculation of the cumulative detector fraction (CDF) for the low-angle laser light scattering (LALLS) detector is done using the baseline subtracted peak height (H) of the absolute molecular weight chromatogram. Those values are summed over the entire chromatogram from high to low molecular weight (low to high retention volume, RV) at each data slice (j), essentially integrating the area of the chromatogram. A fraction of the entire molecular weight chromatogram is obtained by ratioing values greater than or equal to 500,000 g/mol to the lowest RV, Equation 8:

[83] $$\boldsymbol{CDF}_{\boldsymbol{LS \geq 500{,}000 MW}} = \frac{\sum_{\boldsymbol{j=RV\ at\ Lowest\ Integrated\ Volume}}^{\boldsymbol{j=RV\ at\ 500{,}000\ MW}} \boldsymbol{Hj}}{\sum_{\boldsymbol{j=\ RV\ at\ Lowest\ Integrated\ Volume}}^{\boldsymbol{j=RV\ at\ Highest\ Integrated\ Volume}} \boldsymbol{Hj}} \quad \text{(Eq. 8).}$$

[84] Vinyl end group calculation method

[85] To determine vinyl count, approximately 7 mg of polymer sample was loaded into a 5mm NMR tube with 0.6 ml tetrachloroethane-d_2 with 0.008 M chromium(III) acetylacetonate. The tube was purged with N_2, and the cap was secured with Teflon tape. The prepared sample tube was heated in a heating block set at 125 °C and repeatedly vortexed until a homogeneous solution was achieved evidenced by consistent flow when the tube was tipped horizontally. The finished sample was inserted into a Bruker AVANCE 600 MHz system equipped with a 10 mm high-temperature cryo-probe set at 120 °C. The acquisition parameters for the ^{1}H NMR spectra are: 90 degree pulse, 1.8 second acquisition time, 10 seconds relaxation delay, center of spectrum set at 2 ppm, spectral width of 20 ppm and 128 scans for signal averaging. The resulting raw FID was exponential multiplied, Fourier transformed, phased, baseline corrected, and integrated using MNOVA software.

[86] Melt Strength (MS)

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

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

[89] Dart Strength

[90] ASTM D1709 Dart Drop

[91] 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.

[92] After the film is produce, 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.

[93] 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.

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

[95] Instrumented Dart Impact

[96] 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).

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

[98] Polymer Defect Count

[99] The 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 mm^2) per 24.6 cm^3 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.

[100] 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.

EXAMPLES

[101] 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.

[102] Resins

[103] The following resins in Table 1 were utilized in the Examples.

[104] Table 1: Resin Properties

Material	**I_2 (g/10 min)**	**Density (g/cm^3)**	**CDF_{LS} (≥500,000)**	**LCBf - LogM 4.5-5.8**	**Vinyls / 1000 Carbons**	**Melt Strength (cN)**	**3.9 / I2 + 1.4**
PCR Resin 1	2.00	0.918	-	-	-	-	
Comparative Virgin Resin C1	0.85	0.918	14	0.07	0.178	4.40	5.99
Comparative Virgin Resin C2	1.00	0.920	26.8	0.00	0.338	3.2	5.30
Virgin Resin 1	0.50	0.917	22.2	0.04	0.069	10.4	9.20
Virgin Resin 2	0.82	0.920	9.7	0.06		9.53	6.16

[105] PCR Resin 1 is AVANGARD™ NATURA PCR-LDPCR-100, a PCR commercially available from Avangard Innovative LP, Houston, Texas.

[106] The procedure to produce Comparative Virgin Resin C1 may be found in Published PCT Application No. WO 2015/200740.

[107] The procedure to produce the Comparative Virgin Resin C2 may be found in Published PCT Application No. WO 2012/166469.

[108] The Inventive Virgin Resins 1 and 2 were produced as follows:

[109] Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked Isopar E commercially available from ExxonMobil Corporation) were purified with molecular sieves before introduction into the reaction environment. Hydrogen was supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure. The solvent and comonomer (1-octene) feed are pressurized via a mechanical positive displacement pump to above reaction pressure. As shown in Table 4, cocatalysts 2 and 3 are used as impurity scavengers and/or catalyst activators. The individual catalyst components (precatalyst or cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (Isopar E) and pressured to above reaction pressure. Cocatalyst 1 was used at a 1.2 ratio to catalyst metal unless otherwise specified. All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems.

[110] Continuous Reactor Procedure for Inventive Virgin Resin 1

[111] The continuous solution polymerizations were carried out in one or more of a CSTR, loop, and/or a plug flow reactor. The CSTR and loop reactors have independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds when specified. A fresh feed for the second reactor may be absent (i.e. fresh solvent, monomers, comonomers and hydrogen may not be added to the second reactor). The plug flow reactor has independent control of catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to the reactors was temperature controlled to anywhere between 5 °C to 50 °C and typically 25 °C. The fresh comonomer feed to the polymerization reactor was fed in with the solvent feed. The fresh solvent feed was controlled typically with each injector receiving half of the total fresh feed mass flow. The cocatalyst was fed based on a calculated specified molar ratio to the procatalysts. Immediately following each fresh injection location, the feed streams were mixed with the circulating polymerization reactor contents with static mixing elements. The ratio of the catalyst feeds was adjusted to obtain the desired polymer melt index, density, and melt strength. The effluent from the polymerization reactor system (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits and passes through a control valve (responsible for maintaining the pressure of the reactor system at a specified target). As the stream exits the reactor it was contacted with water to stop the reaction. In addition, various additives, such

as antioxidants, could be added at this point. The stream then went through another set of static mixing elements to evenly disperse the catalyst kill and additives.

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

[113] The specific processing parameters are provided in Table 2. The catalysts and cocatalysts used are provided in Table 4. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram. PE Component A and PE Component B were compounded as described in the compounding process below.

[114] Table 2: Process details for PE Component A and PE Component B used to make Virgin resin 1

Sample		**PE Component A**	**PA Component B**
Reactor Configuration	Type	Setup 1: Single CSTR Reactor	Setup 1: Dual Series CSTR + Loop
Comonomer type	Type	1-octene	1-octene
First Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	7.4	5.1
First Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.590	0.265
First Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.3E-04	1.9E-05
First Reactor Temperature	°C	160	190
First Reactor Pressure	barg	41	41
First Reactor Ethylene Conversion	%	85.3	80.4
First Reactor Catalyst	Type	A	B
First Reactor Co-Catalyst 1	Type	1	3
First Reactor Co-Catalyst 2	Type	2	None
First Reactor Co-Catalyst 1 to Catalyst Molar Ratio (Cocatalyst to Catalyst Metal ratio)	Ratio	1.2	N/A

Sample		PE Component A	PA Component B
First Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	10.0	2350
First Reactor Residence Time	min	16.3	7.5
Percentage of Total Ethylene Feed to First Reactor	**wt%**	100	50
Second Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	N/A	0.5
Second Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	N/A	0.27
Second Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	N/A	1.9E-05
Second Reactor Temperature	°C	N/A	190
Second Reactor Pressure	barg	N/A	8
Second Reactor Ethylene Conversion	%	N/A	57.4
Second Reactor Catalyst	Type	None	D
Second Reactor Co-Catalyst 1	Type	None	None
Second Reactor Co-Catalyst 2	Type	None	None
Second Reactor Co-Catalyst 1 to Catalyst Molar Ratio (Cocatalyst to Catalyst Metal ratio)	Ratio	N/A	N/A
Second Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	N/A	N/A
Second Reactor Residence Time	min	N/A	6.7

[115] Continuous Reactor Procedure for Inventive Virgin Resin 2

[116] A two reactor system was used in a series configuration. The first reactor was a continuous solution polymerization reactor consisting of a liquid full, adiabatic, continuously stirred tank reactor (CSTR). Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds was possible. The total fresh feed stream to the second reactor (solvent, monomer, comonomer, and hydrogen) was temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the second polymerization reactor was injected into the reactor at one location. The catalyst components were injected into the second polymerization reactor separate from the fresh feed. The primary catalyst component feed was computer controlled to maintain the reactor monomer conversion at the specified value. The cocatalyst component(s) were fed based on molar ratios to the primary catalyst component. Mixing of the second reactor was provided by an agitator. The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and

polymer) exited the first reactor loop and is added to the second reactor separate from the optional fresh feed and separate from the catalyst feed components.

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

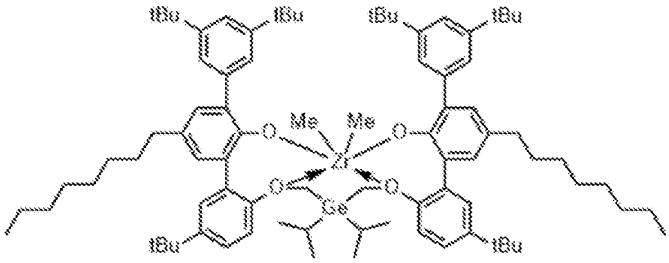
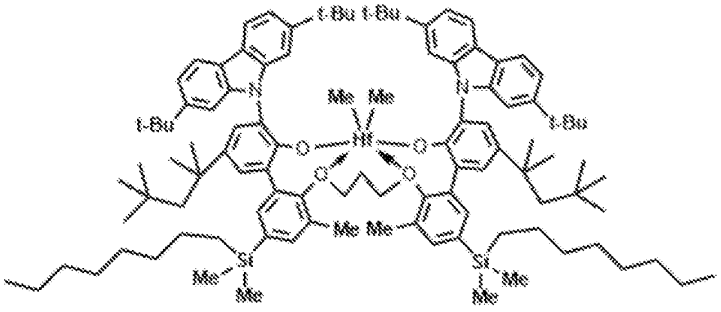
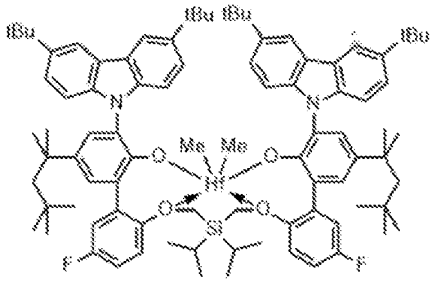
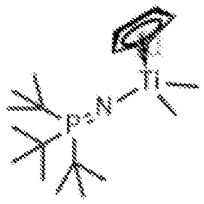
[118] The second reactor effluent entered a zone where it is deactivated with the addition of and reaction with a suitable reagent (water). Antioxident addition can also occur at this same addition point. Following catalyst deactivation and additive addition, the reactor effluent entered a devolatization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

[119] The specific processing parameters are provided in Table 3. The catalysts and cocatalysts used are provided in Table 4. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram.

[120] Table 3: Preparation of Virgin Resin 2.

Reactor Configuration	Type	Dual Parallel Reactors
Comonomer type	Type	1-octene
First Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	5.7
First Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.09
First Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	3.8E-05
First Reactor Temperature	°C	190
First Reactor Pressure	barg	28
First Reactor Ethylene Conversion	%	96.7
First Reactor Catalyst 1	Type	D
First Reactor Catalyst 2	Type	C
First Reactor Catalyst 2 molar ratio: (Catalyst 1)mol/(Catalyst 1+Catalyst 2)mol * 100	ratio	3.7
First Reactor Co-Catalyst 1 Type	Type	1
First Reactor Co-Catalyst 2 Type	Type	2
First Reactor Co-Catalyst 1 to Catalyst Molar Ratio (Cocatalyst to Catalyst Metal ratio)	Ratio	1.3
First Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	14.7
First Reactor [Al] from Co-Catalyst 2	ppmw	0.53
First Reactor Residence Time	min	11.7
Percentage of Total Ethylene Feed to First Reactor	wt%	44.7
Second Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	8.5
Second Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.535
Second Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	1.8E-04
Second Reactor Temperature	°C	160
Second Reactor Pressure	barg	28
Second Reactor Ethylene Conversion	%	12.5
Second Reactor Catalyst 1	Type	A
Second Reactor Co-Catalyst 1 Type	Type	1
Second Reactor Co-Catalyst 2 Type	Type	2
Second Reactor Co-Catalyst 1 to Catalyst Molar Ratio (Cocatalyst to Catalyst Metal ratio)	Ratio	1.2
Second Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	13.4
Second Reactor Residence Time	min	7.4

[121] Table 4: Catalysts and Cocatalysts

Catalyst Name	Catalyst Structure
Catalyst A	
Catalyst B	
Catalyst C	
Catalyst D	
Cocatalyst 1	A mixture of methyldi(C_{14-18} alkyl)ammonium salts of tetrakis(pentafluorophenyl)borate, prepared by reaction of a long chain trialkylamine (Armeen™ M2HT, available from Akzo-Nobel, Inc.), HCl and $Li[B(C_6F_5)_4]$, substantially as disclosed in USP 5,919,983, Ex. 2 (no further purification performed) (Boulder Scientific)

Catalyst Name	Catalyst Structure
Cocatalyst 2	Modified methylalumoxane (MMAO) Type 3A (no further purification performed). Commercially available from Nouryon.
Cocatalyst 3	Hydrocarbyl-modified methylaluminoxane, specifically modified with n-octyl substituents such that the methyl:n-octyl ratio is approximately 6:1 and containing 10-20% trialkyl aluminum species. Commercially available from Nouryon

[122] Compounding

[123] The following compounding process was used for mixing PE Component A and PE Component B of Virgin Resin 1. Additionally, for analytical testing, such as measuring of melt strength of PCR and virgin resin blends as shown in Table 5, the PCR and virgin blends were compounded according to the following process.

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

[125] Blown Film Fabrication

[126] When making the blown films, the virgin and PCR resins were blended in the blow film extruder described 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 182 °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 40 hrs at 23 (+/-2) °C and 50 (+/-10) % R.H. per ASTM D618 (Procedure A).

[127] Table 5: Instrumented dart impact (IDI) Measurement

PCR wt%	Virgin Resin 1		Virgin Resin 2		Comp. C1	
	Melt Strength (cN)	**IDI - Total Energy (J)**	**Melt Strength (cN)**	**IDI - Total Energy (J)**	**Melt Strength (cN)**	**IDI - Total Energy (J)**
0	10.4	6.30	9.53	1.73	4.40	5.95
25	7.40	1.40	6.16	0.66	2.34	1.32
50	5.53	0.63	5.03	0.41	2.96	0.55

[128] In Table 5, the instrumented dart impact (IDI) resistance of the films comprising the films are recorded. When PCR is incorporated into the comparative and inventive resins, the IDI decreases. However, the melt strength of the inventive resins does not suffer the significant drop in melt strength that the comparative resins do. Therefore, the inventive examples provide the advantage of increasing melt strength without the need for LDPE, while also maintaining IDI.

[129] Defect Count Measurement

[130] Blown films 2 mil thick were produced for Defect Count measurement 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 ± 15% by adjusting the nip roller speed. The films are wound up into a roll.

[131] Table 6: Defect Count

	Defect count (mm^2 defects / 24.6 cm^3 film)		
PCR wt%	Virgin Resin 1	Virgin Resin 2	Comp. C1
0	10.4	49.2	6.72
25	350	429	990
50	1070	1100	1840
75	1750	1640	2280

[132] As shown in Table 6, the films including inventive virgin resins 1 and 2 include a much lower defect count as PCR is increased up to 75 wt.% as compared to Comparative C1.

CLAIMS

1. A polymer blend comprising:

virgin multimodal ethylene-based copolymer, the virgin multimodal ethylene-based copolymer being the polymerized reaction product of ethylene and one or more C_3-C_{14} olefinic comonomers, wherein the virgin multimodal ethylene-based copolymer comprises:

a melt index (I_2) of from 0.5 g/10 minutes (g/10 min) to 10.0 g/10 min, when measured according to ASTM D-1238 at 190 °C and 2.16 kg;

a melt strength (MS) $\geq 3.9/I_2 + 1.4$, 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

a light scattering cumulative detector fraction (CDF_{LS}) from 8% to 50%, wherein the CDF_{LS} is computed by measuring the area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using Gel Permeation Chromatography (GPC); and

recycled ethylene-based polymer comprising post consumer recycled (PCR) ethylene-based polymer, post-industrial recycled (PIR) or combinations of PCR and PIR.

2. The polymer blend of claim 1, wherein the virgin multimodal ethylene-based copolymer has a long-chain branching amount from 0.03 to 0.900 as derived from the concentration of vinyl groups in the produced expressed in vinyls/1,000 carbon atoms.

3. The polymer blend of claims 1 or 2, wherein the virgin multimodal ethylene-based copolymer has a density of from 0.900 g/cc to 0.940 g/cc measured according to ASTM D792.

4. The polymer blend of claims 1 or 3, wherein the I_2 of the virgin multimodal ethylene-based copolymer is from 0.5 to 2 g/10 mins.

5. The polymer blend of any one of claims 1 to 4, wherein the MS of the virgin multimodal ethylene-based copolymer is at least 8 cN.

6. The polymer blend of any of claims 1 to 5, wherein the recycled ethylene-based polymer comprises PCR having a density of 0.900 to 0.930 g/cc and a melt index (I_2) of 0.3 to 3 dg/min.

7. The polymer blend of any one of claims 1 to 6, wherein the CDF_{LS} is from 8 to 25%.

8. The polymer blend of any one of claims 1 to 7, wherein the virgin multimodal ethylene-based copolymer has less than 0.100 vinyls/1,000 carbon atoms.

9. A film comprising the polymer blend of any one of claims 1 to 8, wherein the film is a monolayer or multilayer film.

10. The film of claim 9, wherein the film has a defect count of less than 1000 as measured according to GI400 (mm^2 defect area per 24.6 cm^3 film volume).

11. An article comprising the film of claims 9 or 10.