manufacture, use, and performance of prior LLDPEs made with metallocene catalyst ("prior MCN-LLDPE"). The B-LLDPE copolymer of the present disclosure further addresses the need in the manufacture, use, and performance of resin blends that include LLDPEs made with Ziegler-Natta catalyst and the prior MCN-LLDPE. For example, relative to processability of prior LLDPEs made with Ziegler-Natta catalyst ("prior ZN-LLDPE"), prior MCN-LLDPEs have inferior processability. For example, during extrusion of the prior MCN-LLDPE, the extruder barrel pressure is higher than during extrusion of prior ZN-LLDPE. Also, prior MCN-LLDPEs may have insufficient sealability (e.g., hot seal/hot tack may be too weak) relative to prior ZN-LLDPE. Other processability drawbacks of prior MCN-LLDPEs may include tan delta values that are too high, narrow z-average molecular weight over weight average molecular weight (Mz/Mw) value range, molecular weight distributions (MWD), e.g., M_w/M_n, measured by GPC, that are too narrow, and shear thinning index values that are too low.

[0009] The B-LLDPE copolymers of the present disclosure provide a technical solution to many of the above problems, where the B-LLDPE copolymer has at least one processability characteristic similar to that of an unblended monomodal ZN-LLDPE and at least one stiffness/mechanical property similar to that of an unblended monomodal MCN-LLDPE. The B-LLDPE copolymer is made with a bimodal catalyst system, where products made therefrom, methods of making and using same, and articles containing same are provided herein. The B-LLDPE copolymer has a combination of improved properties comprising at least one processability characteristic similar to that of an unblended monomodal ZN-LLDPE and a dart impact property similar to that of an unblended monomodal MCN-LLDPE.

[0010] In some aspects the B-LLDPE copolymer is characterized by a density from 0.8900 to 0.9300 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B; a melt index (I_2) from 0.1 grams per 10 minutes (g/10 min.) to 5 g/10 min., measured according to the Melt Index Test Method at 190 ^oC and 2.16 kilograms according to ASTM D1238-13; a M_Z from 600,000 to 1,200,000 grams per mole (g/mol), measured according to the Gel Permeation Chromatography (GPC) Test Method; and a hexane extractables content present in a value of up to 2.6 wt.% as measured according to ASTM D-5227:95. In one aspect, there is provided a bimodal linear low density polyethylene copolymer comprising: a density from 0.8900 to 0.9300 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B; a melt index (I_2) from 0.1 grams per 10 minutes (g/10 min.) to 5 g/10 min., measured according to the Melt Index Test Method at 190 ^oC and 2.16 kilograms according

to ASTM D1238-13; a M_Z from 600,000 to 1,200,000 grams per mole (g/mol), measured according to a Gel Permeation Chromatography (GPC) Test Method; and a hexane extractables content present in a value of up to 2.6 wt.% as measured according to ASTM D-5227:95, wherein the bimodal linear low density polyethylene copolymer is made using a bimodal catalyst system comprsising bis(2-pentamethylphenylamido)ethylamine zirconium complex. The B-LLDPE copolymer is further characterized by having a first melt flow ratio (I_{21}/I_2) from 25 to 65, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^oC and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13. In an additional aspect, the B-LLDPE copolymer is characterized by having a first melt flow ratio (I_{21}/I_2) from

30 to 50, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^{o}C and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13. For the various aspects, the B-LLDPE copolymer has a first molecular weight ratio (M_Z/M_W) from 3.5 to 5.5, measured according to the GPC Test Method, wherein M_Z is z-average molecular weight and M_W is weight-average molecular weight.

[0011] In an additional example, the B-LLDPE copolymer is further characterized in that the I_2 is from 0.30 g/10 min. to 0.9 g/10 min., measured according to the Melt Index Test Method at 190 ^{o}C and 2.16 kilograms according to ASTM D1238-13; and the density is from 0.91 to 0.92 g/cm^3 measured according to ASTM D792-13, Method B. Aspects of the B-LLDPE copolymer are further characterized as having a tan delta (tan δ) from 3 to 6, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta (Tan δ) Test Method. This additional example can further include a tan δ from 5.8 to 6.2, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta Test Method, a density from 0.916 to 0.919 g/cm^3 measured according to ASTM D792-13, Method, the M_Z/M_W is 4.9 to 5.2, measured according to the GPC Test Method, the melt index (I_2) from 0.8 grams per 10 minutes (g/10 min.) to 0.9 g/10 min., measured according to the Melt Index Test Method at 190 ^{o}C and 2.16 kilograms according to ASTM D1238-13; and a melt flow ratio (I_{21}/I_2) from 40 to 50, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^{o}C and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13. Alternatively, this additional example can further include a tan δ from 2.8 to 3.2, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta Test Method, a density from 0.916 to 0.919 g/cm^3 measured according to ASTM D792-13, Method, the M_Z/M_W is 3.8 to 4.4, measured according to the GPC Test Method, the melt index (I_2) from 0.3 grams per 10 minutes (g/10 min.) to 0.4 g/10 min., measured according to the Melt Index Test Method at 190 ^{o}C and 2.16 kilograms according to ASTM D1238-13; and a melt flow ratio (I_{21}/I_2) from 30 to 35, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^{o}C and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13. In a further example, each of the B-LLDPE copolymers provided herein has a flow index ratio (I_{21}/I_5) from 5 to 20, measured according to the Flow Index Test Method

and the Flow Rate Test Method at 190 ^{o}C and 21.6 and 5.0 kilograms, respectively, according to ASTM D1238-13.

[0012] In a further example, each of the B-LLDPE copolymers provided herein has a number of short chain branches (SCB) per 1000 carbon atoms, measured according to the GCP Test Method, that is greater at Mw than at Mn. In an additional example, the B-LLDPE copolymers provided herein have a SCB per 1000 C that is 20 to 110 percent greater at Mw than at Mn.

[0013] The examples of the B-LLDPE copolymers provided herein include a comonomer used in forming the B-LLDPE copolymer that is selected from 1-hexene, 1-butene or a combination thereof.

[0014] The present disclosure also includes, in another aspect, a manufactured article comprising a shaped form of the B-LLDPE copolymers provided herein. The present disclosure also includes, in another aspect, a film formed from the B-LLDPE copolymers provided herein. For such aspect, a film produced solely of the B-LLDPE copolymer having a thickness of 25.4 micrometer (1 thousandth of an inch) has an average dart impact resistance of 900 grams (g) to 1300 g as measured according to ASTM D1709 16a. For such aspect, the film also has a normalized cross direction (CD) Elmendorf tear of 600 to 900 gf measured according to ASTM D1922-09, Standard Test Methods for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method, Type B constant radius. For such aspect, the film further has an Elmendorf Tear Ratio (MD/CD) of 0.3 to 0.4, wherein a normalized tear in a cross direction (CD) and a machine direction (MD) are measured according to ASTM D 1922-09, *Standard Test Methods for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method,* Type B (constant radius). For the such aspect, the film provided herein is for packaging of food products. The present disclosure also provides for a process for producing the film provided herein through a casting or a blow extruding process.

[0015] Aspects of the present disclosure also include a method of making the B-LLDPE copolymer as provided herein, where the method comprises contacting ethylene ("C_2") and a comonomer ("C_x") selected from 1-butene (C_x=C_4), 1-hexene (C_x=C_6), or both (C_x=C_4 and C_6) at a comonomer-to-ethylene (C_x/C_2) molar ratio of 0.005 to 0.30 with the bimodal catalyst system comprising a (1,3-dimethyl-tetrahydroindenyl)(methylcyclopentadienyl) zirconium complex and the bis(2-pentamethylphenylamido)ethyl)amine zirconium complex in the presence of molecular hydrogen gas (H_2) at a hydrogen-to-ethylene (H_2/C_2) molar ratio from 0.001 to less than 0.030, all in a single gas phase polymerization reactor containing a fluidized

resin bed at a temperature from 70 °C to 90 °C, thereby making the bimodal linear low density polyethylene copolymer. For such aspect, the method can use a H_2/C_2 molar ratio from 0.006 to 0.015. The bimodal catalyst system can further comprise a metallocene catalyst other than a (1,3-dimethyl-tetrahydroindenyl)(methylcyclopentadienyl)zirconium complex.

Drawings

[0016] Figure (Fig.) 1 contains drawings of formulae of (pro)catalysts.

[0017] Figure (Fig.) 2 Molecular weight and short chain branch distribution for IE1.

Detailed Description

[0018] The Summary, claims and Abstract are incorporated here by reference.

[0019] The bimodal linear low density polyethylene copolymer (B-LLDPE copolymer) of the present disclosure has at least one improved property such as, for example, at least one improved (increased) processability property and/or at least one improved (increased) stiffness property. The improved processability property may be at least one of decreased extruder barrel pressure, increased sealability (*e.g.*, hot seal/hot tack), decreased tan delta value, and increased shear thinning index value. The improved stiffness property may be at least one of increased Elmendorf tear (CD Tear and/or MD Tear), increased melt strength, increased secant modulus, and increased dart impact strength. In some aspects the B-LLDPE copolymer is not characterized by a worsening of any three, alternatively any two, alternatively any one of the foregoing properties. The B-LLDPE copolymer may be used to make films, sheets and injection molded articles.

[0020] Certain inventive embodiments are described below as numbered aspects for easy cross-referencing. Additional embodiments are described elsewhere herein.

[0021] Aspect 1 - a B-LLDPE copolymer comprising a density from 0.8900 to 0.9300 gram per cubic centimeter (g/cm^3), alternatively from 0.8900 to 0.9295 g/cm^3, alternatively from 0.9000 to 0.9272 g/cm^3, alternatively from 0.9030 to 0.9266 g/cm^3, alternatively from 0.9100 to 0.9200 g/cm^3, alternatively from 0.9160 to 0.9190 g/cm^3 measured according to ASTM D792-13, Method B; a melt index (I_2) from 0.1 grams per 10 minutes (g/10 min.) to 5 g/10 min., alternatively from 0.1 to 3.5 g/10 min., alternatively from 0.1 to 1.5 g/10 min., alternatively from 0.3 to 0.9 g/10 min. alternatively from 0.8 to 0.9 g/10 min., alternatively from 0.3 to 0.4 g/10 min., measured according to the Melt Index (MI) Test Method at 190 ^oC and 2.16 kilograms according to ASTM D1238-13; a M_Z from 600,000 to 1,200,000 grams per mole (g/mol), alternatively from 600,000 to 1,000,000 g/mol, alternatively from 600,000 to 900,000 g/mol, alternatively from 600,000 to 800,000 g/mol, alternatively from 600,000 to 700,000

What is claimed is:

1. A bimodal linear low density polyethylene copolymer comprising:

a density from 0.8900 to 0.9300 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B;

a melt index (I_2) from 0.1 grams per 10 minutes (g/10 min.) to 5 g/10 min., measured according to the Melt Index Test Method at 190 ^oC and 2.16 kilograms according to ASTM D1238-13;

a M_Z from 600,000 to 1,200,000 grams per mole (g/mol), measured according to a Gel Permeation Chromatography (GPC) Test Method; and

a hexane extractables content present in a value of up to 2.6 wt.% as measured according to ASTM D-5227:95, wherein the bimodal linear low density polyethylene copolymer is made using a bimodal catalyst system comprsising bis(2-pentamethylphenylamido)ethylamine zirconium complex.

2. The bimodal linear low density polyethylene copolymer of claim 1 having a melt flow ratio (I_{21}/I_2) from 25 to 65, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^oC and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13; or

having a melt flow ratio (I_{21}/I_2) from 30 to 50, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^oC and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13; or

having a first molecular weight ratio (M_Z/M_W) from 3.5 to 5.5, measured according to the GPC Test Method, wherein M_Z is z-average molecular weight and M_W is weight-average molecular weight.

3. The bimodal linear low density polyethylene copolymer of claim 1 or 2,

wherein the I_2 is from 0.3 g/10 min. to 0.9 g/10 min., measured according to the Melt Index Test Method at 190 ^oC and 2.16 kilograms according to ASTM D1238-13; and

wherein the density is from 0.9100 to 0.9200 g/cm^3 measured according to ASTM D792-13, Method B; or

the bimodal linear low density polyethylene copolymer having a tan delta (tan δ) from 3 to 6, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta Test Method.

4. The bimodal linear low density polyethylene copolymer of claim 1 having:

a tan δ is from 5.8 to 6.2, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta Test Method;

the density is from 0.9160 to 0.9190 g/cm^{3} measured according to ASTM D792-13, Method B;

the M_z/M_w is 4.9 to 5.2, measured according to the GPC Test Method;

the melt index (I_2) from 0.8 grams per 10 minutes (g/10 min.) to 0.9 g/10 min., measured according to the Melt Index Test Method at 190 ^{o}C and 2.16 kilograms according to ASTM D1238-13; and

a melt flow ratio (I_{21}/I_2) from 40 to 50, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^{o}C and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13; or

the bimodal linear low density polyethylene copolymer of claim 1 having:

a tan δ is from 2.8 to 3.2, measured at 190 ^{o}C and a frequency of 0.1000 radians per second (rad/s) according to Tan Delta Test Method;

the density is from 0.9160 to 0.9190 g/cm^{3} measured according to ASTM D792-13, Method B;

the M_z/M_w is 3.8 to 4.4, measured according to the GPC Test Method;

the melt index (I_2) from 0.3 grams per 10 minutes (g/10 min.) to 0.4 g/10 min., measured according to the Melt Index Test Method at 190 ^{o}C and 2.16 kilograms according to ASTM D1238-13; and

a melt flow ratio (I_{21}/I_2) from 30 to 35, measured according to the Flow Index Test Method and the Melt Index Test Method at 190 ^{o}C and 21.6 and 2.16 kilograms, respectively, according to ASTM D1238-13.

5. The bimodal linear low density polyethylene copolymer of any one of claims 1-8 having a flow index ratio (I_{21}/I_5) from 5 to 20, measured according to the Flow Index Test

Method and the Flow Rate Test Method at 190 ^{o}C and 21.6 and 5.0 kilograms, respectively, according to ASTM D1238-13; or

wherein a number of short chain branches per 1000 carbon atoms measured according to the GCP Test Method is greater at Mw than at Mn; or

where the SCB per 1000 C is 20 to 110 percent greater at Mw than at Mn; or

wherein a comonomer used in forming the bimodal linear low density polyethylene copolymer is selected from 1-hexene, 1-butene or a combination thereof.

6. A manufactured article comprising a shaped form of the bimodal linear low density polyethylene copolymer of any one of claims 1 to 5.

7. A film formed from the bimodal linear low density polyethylene copolymer of any one of claims 1 to 5.

8. The film of claim 7, wherein the film produced solely of the bimodal linear low density polyethylene copolymer having a thickness of 25.4 micrometer (1 thousandth of an inch) has an average dart impact resistance of 900 grams (g) to 1300 g as measured according to ASTM D1709 16a; or

wherein the film has a normalized cross direction Elmendorf tear of 600 to 900 gf measured according to ASTM D1922-09, Standard Test Methods for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method, Type B constant radius; or

wherein the film having a thickness of 25 micrometer has an Elmendorf Tear Ratio (MD/CD) of 0.3 to 0.4, wherein a normalized tear in a cross direction (CD) and a machine direction are measured according to ASTM D 1922-09, *Standard Test Methods for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method,* Type B (constant radius).

9. A method of making the bimodal linear low density polyethylene copolymer of any one of claims 1-5, the method comprising contacting ethylene ("C_2") and a comonomer ("C_x") selected from 1-butene (C_x = C_4), 1-hexene (C_x = C_6), or both (C_x = C_4 and C_6) at a comonomer-to-ethylene (C_x/C_2) molar ratio of 0.005 to 0.30 with the bimodal catalyst system comprising a (1,3-dimethyl-tetrahydroindenyl)(methylcyclopentadienyl) zirconium

complex and the bis(2-pentamethylphenylamido)ethyl)amine zirconium complex in the presence of molecular hydrogen gas (H_2) at a hydrogen-to-ethylene (H_2/C_2) molar ratio from 0.001 to less than 0.030, all in a single gas phase polymerization reactor containing a fluidized resin bed at a temperature from 70 °C to 90 °C, thereby making the bimodal linear low density polyethylene copolymer.

10. The method of claim 9, wherein the H_2/C_2 molar ratio is from 0.006 to 0.015; or wherein the bimodal catalyst system comprises a metallocene catalyst other than a (1,3-dimethyl-tetrahydroindenyl)(methylcyclopentadienyl)zirconium complex.