BIMODAL POLYETHYLENE COPOLYMER COMPOSITION AND PIPE MADE THEREOF

FIELD

[0001] Polyethylene copolymer compositions, pipes, and related methods.

INTRODUCTION

[0002] Patent application publications and patents in or about the field include US 2016/0068623 A1; US 2016/0297907 A1; WO 2016/188703 A1; WO 2017/009058 A1; WO 2017/093008 A1; WO 2017/132092 A1; EP1985660B2' EP2285896B1; US 5,332,706; US 5,882,750; US 6,989,344 B2; US 7,078,467 B1; US 7,090,927 B2; US 7,157,531 B2; US 7,223,825 B2; US 7,300,988 B2; US 8,227,552 B2; US 8,497,329 B2; and US 9,051,458 B2.

SUMMARY

[0003] A bimodal ethylene-*co*-1-hexene copolymer composition consisting essentially of a higher molecular weight (HMW) component and a lower molecular weight (LMW) component and, when in melted form at 190 degrees Celsius (° C.), is characterized by a melt property performance defined by a combination of melt flow index(5 kg), melt strength, and, optionally, shear thinning properties, and, when in solid form, is characterized by a slow crack growth property performance defined by a combination of strain hardening modulus and accelerated full-notch creep test (FNCT) performance ("the bimodal ethylene-*co*-1-hexene copolymer composition"). With "consisting essentially of", the bimodal ethylene-*co*-1-hexene copolymer composition is free of a distinct third or more component as determined by gel permeation chromatography (GPC) measured according to the GPC Test Method. For example, the bimodal ethylene-*co*-1-hexene copolymer composition is not trimodal or tetramodal.

[0003a] In one aspect, the present disclosure relates to a bimodal ethylene-*co*-1-hexene copolymer composition having a density from 0.945 to 0.960 gram per cubic centimeter (g/cm^3), measured according to ASTM D792-13, Method B; a molecular mass dispersity (M_W/M_n), $Đ_M$, from 11.0 to 25.0, wherein M_W and M_n are measured according to the Gel Permeation Chromatography (GPC) Test Method; and consisting essentially of a higher molecular weight ethylene-*co*-1-hexene copolymer component (HMW component), having a molecular weight distribution (Mw/Mn) greater than 3.75 (> 3.75), and a lower molecular weight polyethylene homopolymer or a lower molecular weight ethylene-*co*-1-hexene copolymer component (LMW component), wherein the LMW component has a molecular weight distribution (Mw/Mn) from 2.75 to 3.35; and having a component fraction split characterized by a weight fraction of the HMW component from 35.0 to 65.0 wt% and a weight fraction of the LMW component fraction from 65.0 to 35.0 wt%, respectively, of the

combined weight of the HMW and LMW components, measured according to the GPC Test Method; and wherein when in melted form at 190° C., the bimodal ethylene-*co*-1-hexene copolymer composition is characterized by properties (a), (b), and optionally (c): (a) a melt flow index(5 kg) (I_5 or MFI_5) from 0.15 to 0.30 gram per 10 minutes (g/10 min.), (b) peak melt strength from 18 to 29 centiNewtons (cN), and, optionally, (c) shear thinning index, $\eta_{0.01}/\eta_{100}$, from 96 to 125; and when in solid form the bimodal ethylene-*co*-1-hexene copolymer composition is characterized by properties (d) and (e): (d) strain hardening modulus from 50.0 to 75 megapascals (MPa) and (e) accelerated full-notch creep test (FNCT) performance from 401 to 700.0 hours; wherein the melt flow index (5 kg) is measured according to ASTM D1238-13 (190° C., 5.0 kg), the shear thinning index is measured according to Shear Thinning Index Test Method (190° C.), the peak melt strength is measured at the highest peak in a plot of melt strength versus a range of velocity from 10 to 50 millimeters per second (mm/s) according to Melt Strength Test Method, the strain hardening modulus is measured according to ISO 18488:2015, and the accelerated FNCT performance is measured according to ISO 16770:2004 at 90° C. and under an actual stress of 5.0 MPa in 2 weight percent (wt%) lauramine oxide in water.

[0004] A method of synthesizing the bimodal ethylene-*co*-1-hexene copolymer composition, the method consisting essentially of polymerizing ethylene (monomer) and 1-hexene (comonomer) with a single bimodal catalyst system in a single fluidized-bed, gas phase polymerization (FB-GPP) reactor under effective operating conditions, thereby making the bimodal ethylene-*co*-1-hexene copolymer composition. With “consisting essentially of”, the method is free of Ziegler-Natta catalysts and chrome catalysts (containing Cr, e.g., chromium oxide catalysts), and the polymerizing is carried out in a single reactor (i.e., in the FB-GPP reactor), and the operating conditions are effective for making the bimodal ethylene-*co*-1-hexene copolymer composition with the combination of melt index(5) (I_5), melt strength, and, optionally, shear thinning properties and the combination of strain hardening modulus and accelerated FNCT performance. The effective operating conditions include reactor bed

temperature, hydrogen-to-ethylene (H_2/C_2) molar ratio, and 1-hexene-to-ethylene (C_6/C_2) molar ratio. Other than that, the method is not particularly limited.

[0004a] In another aspect, the present disclosure relates to a method of synthesizing the bimodal ethylene-*co*-1-hexene copolymer composition as described herein, the method consisting essentially of copolymerizing ethylene and 1-hexene, and copolymerizing fresh ethylene and, optionally, fresh 1-hexene, with a combination of a bimodal catalyst system and a trim catalyst in the presence of molecular hydrogen gas and, optionally, an induced condensing agent in one polymerization reactor under effective polymerizing conditions to give an initial bimodal ethylene-*co*-1-hexene copolymer composition; wherein the bimodal catalyst system is made by contacting a first activator with bis(2-(pentamethylphenylamido)ethyl)-amine zirconium dibenzyl and a (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl; wherein the trim catalyst is made by contacting a second activator with (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl; wherein the first and second activators are the same or different; and wherein the effective polymerizing conditions comprise a reactor bed temperature from 90 degrees (°) to 110° Celsius (C.); a molar ratio of the molecular hydrogen gas to the ethylene from 0.001 to 0.0050; and a molar ratio of the 1-hexene to the ethylene from 0.00450 to 0.01000.

[0005] A pipe consisting essentially of the bimodal ethylene-*co*-1-hexene copolymer composition. The pipe is characterized by enhanced (increased) inhibition of slow crack growth as measured by accelerated FNCT performance. With “consisting essentially of”, the film is free of other polyolefin polymers, but otherwise its constituents are not particularly limited.

[0005a] In another aspect, the present disclosure relates to a pipe consisting essentially of the bimodal ethylene-*co*-1-hexene copolymer composition as described herein.

[0006] A method of making a pipe, the method comprising melting the bimodal ethylene-*co*-1-hexene copolymer composition to give a melt thereof; extruding the melt into an initial pipe; optionally resizing the pipe; and cooling the initial or resized pipe. The method may be conducted using a pipe forming machine.

[0006a] In another aspect, the present disclosure relates to a method of making a pipe, the method comprising method of making a pipe, the method comprising steps (A), (B1) or (B2), optionally (C), and (D): (A) melting the bimodal ethylene-*co*-1-hexene copolymer composition as described herein to give a melt thereof; (B1) extruding the melt through an annular die configured for forming a cylinder so as to make an initial solid wall cylinder of the bimodal ethylene-*co*-1-hexene copolymer composition or (B2) extruding and spirally winding the melt

around a mandrel configured for forming an unsealed-seam profile wall so as to make an unsealed-seam profile wall, and heat-fusing the unsealed seam of the unsealed-seam profile wall to make an initial sealed-seam wall cylinder; (C) optionally resizing the initial solid wall cylinder or the initial sealed-seam wall cylinder to make a resized wall cylinder having a different diameter; and (D) cooling the initial solid wall cylinder, the initial sealed-seam wall cylinder, or the resized wall cylinder, thereby making a solid wall pipe or a seam-sealed wall pipe, respectively

[0007] A manufactured article comprising the bimodal ethylene-*co*-1-hexene copolymer composition.

[0007a] In another aspect, the present disclosure relates to a manufactured article comprising the bimodal ethylene-*co*-1-hexene copolymer composition, wherein the manufactured article is not a pipe.

DETAILED DESCRIPTION

[0008] The Summary and Abstract are incorporated here by reference. Certain embodiments are described below as numbered aspects for easy cross-referencing.

[0009] Aspect 1. A bimodal ethylene-*co*-1-hexene copolymer composition having a density from 0.945 to 0.960 gram per cubic centimeter (g/cm^3), measured according to ASTM D792-13, Method B; a molecular mass dispersity (M_w/M_n), $Đ_M$, from 11.0 to 25.0, wherein M_w and M_n are measured according to the Gel Permeation Chromatography (GPC) Test Method; and consisting essentially of a higher molecular weight ethylene-*co*-1-hexene copolymer component (HMW component), having a molecular weight distribution (Mw/Mn) greater than 3.75 (> 3.75), alternatively from 3.76 to 10.0, alternatively 3.80 to 9.40, and either a lower molecular weight polyethylene homopolymer component or a lower molecular weight ethylene-*co*-1-hexene copolymer component (LMW component), wherein the LMW component has a molecular weight distribution (Mw/Mn) from 2.75 to 3.35; and having a component fraction split characterized by a weight fraction of the HMW component from 35.0 to 65.0 wt%, alternatively from 36.0 to 50.0 wt% and a weight fraction of the LMW component fraction from 65.0 to 35.0 wt%, alternatively from 64.0 to 50.0 wt%, respectively, of the combined weight of the HMW and LMW components, measured according to the GPC Test Method; and wherein when in melted form at 190° C., the bimodal ethylene-*co*-1-hexene copolymer composition is characterized by properties (a), (b), and optionally (c): (a) a melt flow index(5 kg) (I_5 or MFI_5) from 0.15 to 0.30 gram per 10 minutes (g/10 min.), (b) peak melt strength from 18 to 29 centiNewtons (cN), and optionally (c) shear thinning index, $\eta_{0.01}/\eta_{100}$, is from 96 to 125; and when in solid form the bimodal ethylene-*co*-1-hexene

CLAIMS

1. A bimodal ethylene-*co*-1-hexene copolymer composition having a density from 0.945 to 0.960 gram per cubic centimeter (g/cm^3), measured according to ASTM D792-13, Method B; a molecular mass dispersity (M_w/M_n), $Đ_M$, from 11.0 to 25.0, wherein M_w and M_n are measured according to the Gel Permeation Chromatography (GPC) Test Method; and consisting essentially of a higher molecular weight ethylene-*co*-1-hexene copolymer component (HMW component), having a molecular weight distribution (Mw/Mn) greater than 3.75 (> 3.75), and a lower molecular weight polyethylene homopolymer or a lower molecular weight ethylene-*co*-1-hexene copolymer component (LMW component), wherein the LMW component has a molecular weight distribution (Mw/Mn) from 2.75 to 3.35; and having a component fraction split characterized by a weight fraction of the HMW component from 35.0 to 65.0 wt% and a weight fraction of the LMW component fraction from 65.0 to 35.0 wt%, respectively, of the combined weight of the HMW and LMW components, measured according to the GPC Test Method; and wherein when in melted form at 190° C., the bimodal ethylene-*co*-1-hexene copolymer composition is characterized by properties (a), (b), and optionally (c): (a) a melt flow index(5 kg) (I_5 or MFI_5) from 0.15 to 0.30 gram per 10 minutes (g/10 min.), (b) peak melt strength from 18 to 29 centiNewtons (cN), and, optionally, (c) shear thinning index, $\eta_{0.01}/\eta_{100}$, from 96 to 125; and when in solid form the bimodal ethylene-*co*-1-hexene copolymer composition is characterized by properties (d) and (e): (d) strain hardening modulus from 50.0 to 75 megapascals (MPa) and (e) accelerated full-notch creep test (FNCT) performance from 401 to 700.0 hours; wherein the melt flow index (5 kg) is measured according to ASTM D1238-13 (190° C., 5.0 kg), the shear thinning index is measured according to Shear Thinning Index Test Method (190° C.), the peak melt strength is measured at the highest peak in a plot of melt strength versus a range of velocity from 10 to 50 millimeters per second (mm/s) according to Melt Strength Test Method, the strain hardening modulus is measured according to ISO 18488:2015, and the accelerated FNCT performance is measured according to ISO 16770:2004 at 90° C. and under an actual stress of 5.0 MPa in 2 weight percent (wt%) lauramine oxide in water.

2. The bimodal ethylene-*co*-1-hexene copolymer composition of claim 1 characterized by any one of property limitations (i) to (viii): (i) the density is from 0.9450 to 0.9590 g/cm^3; (ii) the component fraction split is characterized by a weight fraction of the HMW component from 44.0 to 52.0 wt%; and a weight fraction of the LMW component fraction from 56.0 to 48.0 wt%, respectively, of the combined weight of the HMW and LMW components; (iii) the molecular mass dispersity (M_w/M_n), $Đ_M$, is from 11.0 to 23.0; (iv) the (a) MFI_5 is from 0.15

to 0.24 g/10 min.; (v) the (c) shear thinning index, $\eta_{0.01}/\eta_{100}$, is from 99 to 115; (vi) the (b) peak melt strength is from 20.0 to 28 cN; (vii) the (d) strain hardening modulus is from 55 to 70.0 MPa; and (viii) the (e) accelerated FNCT performance is from 401 to 600.0 hours.

3. The bimodal ethylene-*co*-1-hexene copolymer composition of claim 1 or 2 further characterized by any one of melt property limitations (i) to (iii): (i) a high load melt index from 1 to 10 g/10min., measured according to ASTM D1238-13 (190° C., 21.6 kg, HLMI or I_{21}); (ii) a melt flow ratio I_{21}/I_5 ("MFR5") from 20 to 40, wherein the I_{21} and I_5 values used to calculate the MFR5 are each in g/10 min. and are measured according to ASTM D1238-13 (190° C., 21.6 kg, "I_{21}"; and 190° C., 5.0 kg, "I_5", respectively); (iii) both (i) and (ii).

4. The bimodal ethylene-*co*-1-hexene copolymer composition of any one of claims 1 to 3 further characterized by any one of resin property limitations (i) to (xii): (i) a weight-average molecular weight (M_w) from 300,000 to 400,000 grams per mole (g/mol); (ii) a number-average molecular weight (M_n) from 10,000 to 30,000 grams g/mol; (iii) a z-average molecular weight (M_z) from 2,000,000 to 3,400,000 g/mol; (iv) a butyl branch frequency per 1,000 carbon atoms (bbf/1000C) from 1.2 to 1.5, as measured according to the Butyl Branch Frequency Test Method; and wherein M_w, M_n and M_z are measured according to the GPC Test Method.

5. A method of synthesizing the bimodal ethylene-*co*-1-hexene copolymer composition of any one of claims 1 to 4, the method consisting essentially of copolymerizing ethylene and 1-hexene, and copolymerizing fresh ethylene and, optionally, fresh 1-hexene, with a combination of a bimodal catalyst system and a trim catalyst in the presence of molecular hydrogen gas and, optionally, an induced condensing agent in one polymerization reactor under effective polymerizing conditions to give an initial bimodal ethylene-*co*-1-hexene copolymer composition; wherein the bimodal catalyst system is made by contacting a first activator with bis(2-(pentamethylphenylamido)ethyl)-amine zirconium dibenzyl and a (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl; wherein the trim catalyst is made by contacting a second activator with (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl; wherein the first and second activators are the same or different; and wherein the effective polymerizing conditions comprise a ~~reaction~~ reactor bed temperature from 90 degrees (°) to 110° Celsius (C.); a molar ratio of the molecular hydrogen gas to the ethylene from 0.001 to 0.0050; and a molar ratio of the 1-hexene to the ethylene from 0.00450 to 0.01000.

6. The method of claim 5 further consisting essentially of removing the bimodal ethylene-*co*-1-hexene copolymer composition from the reactor to give a removed bimodal ethylene-*co*-1-hexene copolymer composition.

7. A pipe consisting essentially of the bimodal ethylene-*co*-1-hexene copolymer composition of any one of claims 1 to 4.

8. A method of making a pipe, the method comprising method of making a pipe, the method comprising steps (A), (B1) or (B2), optionally (C), and (D): (A) melting the bimodal ethylene-*co*-1-hexene copolymer composition of any one of claims 1 to 4 to give a melt thereof; (B1) extruding the melt through an annular die configured for forming a cylinder so as to make an initial solid wall cylinder of the bimodal ethylene-*co*-1-hexene copolymer composition or (B2) extruding and spirally winding the melt around a mandrel configured for forming an unsealed-seam profile wall so as to make an unsealed-seam profile wall, and heat-fusing the unsealed seam of the unsealed-seam profile wall to make an initial sealed-seam wall cylinder; (C) optionally resizing the initial solid wall cylinder or the initial sealed-seam wall cylinder to make a resized wall cylinder having a different diameter; and (D) cooling the initial solid wall cylinder, the initial sealed-seam wall cylinder, or the resized wall cylinder, thereby making a solid wall pipe or a seam-sealed wall pipe, respectively.

9. A pipe made by the method of claim 8 and consisting essentially of the bimodal ethylene-*co*-1-hexene copolymer composition of any one of claims 1 to 4.

10. A manufactured article comprising the bimodal ethylene-*co*-1-hexene copolymer composition, wherein the manufactured article is not a pipe.