BIMODAL POLYETHYLENE COPOLYMER AND FILM THEREOF

FIELD

[0001] Polyethylene copolymers, films, manufactured articles, and related methods.

INTRODUCTION

[0002] Patent application publications in or about the field include US 2016/0068623 A1; US 2016/0297907 A1; and WO 2017/132092 A1. Patents in or about the field include 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 and US 8,497,329 B2.

SUMMARY

[0003] A bimodal ethylene-*co*-1-butene copolymer 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 space and is useful for making a blown film having a film property space.

[0003a] In one aspect, the present disclosure refers to a bimodal ethylene-*co*-1-butene copolymer consisting essentially of a higher molecular weight (HMW) component and a lower molecular weight (LMW) component and, when in melted form at 190° C., is characterized by a melt property space defined by a combination of high-load melt index ("HLMI" or "I_{21}"), melt flow ratio I_{21}/I_5 ("MFR5"), and melt elasticity (G′/G″@0.1 rad/s) properties, wherein the HLMI is 8.0 to 12.0 grams per 10 minutes (g/10 min.); the MFR5 is 25.0 to 37.0, 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), and the melt elasticity is 0.55 to 0.68, and wherein melt elasticity = G′/G″ determined at 0.1 radian per second (rad/s) according to Melt Elasticity Test Method; and wherein the HMW component has a weight-average molecular weight ($M_{w\text{-}HMW}$) greater than 425,000 g/mol, measured according to the GPC Test Method; and wherein the bimodal ethylene-*co*-1-butene copolymer has (i) a density from 0.9410 to 0.9550 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B; (ii) a component fraction split characterized by a weight fraction of the HMW component from 50.0 to 60.0 wt%; and a weight fraction of the LMW component fraction is from 50.0 to 40.0 wt% of the combined weight of the HMW and LMW components, measured according to the Gel Permeation Chromatography (GPC) Test Method; (iii) a component molecular weight spread characterized by a ratio of the weight-average molecular weight of the HMW component ($M_{w\text{-}HMW}$) to the weight-average molecular weight of the LMW component ($M_{w\text{-}LMW}$) from 35.0 to 45.0, measured according to the GPC Test Method; (iv) a molecular mass dispersity

(M_W/M_n), $Đ_M$, from 34 to 44, wherein M_W and M_n are measured according to the GPC Test Method; (v) the $M_{W\text{-}HMW}$ is from 435,000 to 465,000 g/mol measured according to the GPC Test Method; (vi) a number-average molecular weight (M_n) from 6,900.0 to 8,000.0 g/mol; (vii) a weight-average molecular weight (M_W) from 250,000.0 to 300,000.0 g/mol; (viii) a z-average molecular weight (M_Z) from 1,800,000.0 to 2,500,000.0 g/mol.

[0004] A method of synthesizing the bimodal ethylene-*co*-1-butene copolymer; a (blown) film consisting essentially of the bimodal ethylene-*co*-1-butene copolymer ("the film"); and a manufactured article comprising the bimodal ethylene-*co*-1-butene copolymer.

[0004a] In another aspect, the present disclosure refers to a method of synthesizing the bimodal ethylene-*co*-1-butene copolymer as described herein, the method consisting essentially of (a) copolymerizing ethylene (monomer) and 1-butene (comonomer) with a combination of a bimodal catalyst system and a trim catalyst in the presence of molecular hydrogen gas (H_2) and, optionally, an induced condensing agent (ICA) in one polymerization reactor (e.g., one fluidized bed, gas phase polymerization reactor (FB-GPP reactor)) under effective polymerizing conditions to give an initial bimodal ethylene-*co*-1-butene copolymer, (b) removing the initial bimodal ethylene-*co*-1-butene copolymer from the reactor (e.g., the FB-GPP reactor) to give a removed bimodal ethylene-*co*-1-butene copolymer, and (c) oxygen tailoring the removed bimodal ethylene-*co*-1-butene copolymer to give an oxygen-tailored bimodal ethylene-*co*-1-butene copolymer.

[0004b] In another aspect, the present disclosure refers to a manufacture article comprising the bimodal ethylene-*co*-1-butene copolymer as described herein.

[0004c] In another aspect, the present disclosure refers to a film consisting essentially of the bimodal ethylene-*co*-1-butene copolymer as described herein and characterized when at a thickness of 0.013 millimeter or greater as having a dart impact of greater than 290 grams measured by the Dart Impact Test Method.

[0004d] In another aspect, the present disclosure refers to a method of making a blown film, the method comprising extruding a melt of the bimodal ethylene-*co*-1-butene copolymer as described herein through a die configured for forming a bubble so as to make a bubble of the bimodal ethylene-*co*-1-butene copolymer, and blowing (inflating) the bubble with a film-blowing machine, thereby making the blown film.

[0004e] In another aspect, the present disclosure refers to a blown film made by the method as described herein and consisting essentially of the bimodal ethylene-*co*-1-butene copolymer as described herein.

DETAILED DESCRIPTION

[0005] The Summary and Abstract are incorporated here by reference. Certain embodiments are described below as numbered aspects for easy cross-referencing.

[0006] Aspect 1. A bimodal ethylene-*co*-1-butene ("BiEtBu") copolymer consisting essentially of a higher molecular weight (HMW) component and a lower molecular weight (LMW) component and, when in melted form at 190° C., is characterized by a melt property space defined by a combination of high-load melt index ("HLMI" or "I_{21}"), melt flow ratio I_{21}/I_5 ("MFR5"), and melt elasticity (G′/G″@0.1 rad/s) properties, wherein the HLMI is 8.0 to 12.0 grams per 10 minutes (g/10 min.), alternatively 8.1 to 11.0 g/10 min., alternatively 8.1 to 10.4 g/10 min. and is measured according to ASTM D1238-13 (190° C., 21.6 kg); the MFR5 is 25.0 to 37.0, alternatively 26.0 to 36.0, alternatively 27.4 to 33.9 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), and the melt elasticity is 0.55 to 0.68, alternatively 0.56 to 0.66, alternatively 0.57.5 to 0.640, and wherein melt elasticity = G′/G″ determined at 0.1 radian per second (rad/s) according to Melt Elasticity Test Method (described herein); and wherein the HMW component has a weight-average molecular weight ($M_{w\text{-}HMW}$) greater than 425,000 g/mol. The "/" means division. The melt elasticity characterizes the relationship between melt storage modulus (G′) and loss

CLAIMS

1. A bimodal ethylene-*co*-1-butene copolymer consisting essentially of a higher molecular weight (HMW) component and a lower molecular weight (LMW) component and, when in melted form at 190° C., is characterized by a melt property space defined by a combination of high-load melt index ("HLMI" or "I_{21}"), melt flow ratio I_{21}/I_5 ("MFR5"), and melt elasticity (G′/G″@0.1 rad/s) properties, wherein the HLMI is 8.0 to 12.0 grams per 10 minutes (g/10 min.); the MFR5 is 25.0 to 37.0, 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), and the melt elasticity is 0.55 to 0.68, and wherein melt elasticity = G′/G″ determined at 0.1 radian per second (rad/s) according to Melt Elasticity Test Method; and wherein the HMW component has a weight-average molecular weight ($M_{W\text{-}HMW}$) greater than 425,000 g/mol, measured according to the GPC Test Method; and wherein the bimodal ethylene-*co*-1-butene copolymer has (i) a density from 0.9410 to 0.9550 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B; (ii) a component fraction split characterized by a weight fraction of the HMW component from 50.0 to 60.0 wt%; and a weight fraction of the LMW component fraction is from 50.0 to 40.0 wt% of the combined weight of the HMW and LMW components, measured according to the Gel Permeation Chromatography (GPC) Test Method; (iii) a component molecular weight spread characterized by a ratio of the weight-average molecular weight of the HMW component ($M_{W\text{-}HMW}$) to the weight-average molecular weight of the LMW component ($M_{W\text{-}LMW}$) from 35.0 to 45.0, measured according to the GPC Test Method; (iv) a molecular mass dispersity (M_W/M_n), $Đ_M$, from 34 to 44, wherein M_W and M_n are measured according to the GPC Test Method; (v) the $M_{W\text{-}HMW}$ is from 435,000 to 465,000 g/mol measured according to the GPC Test Method; (vi) a number-average molecular weight (M_n) from 6,900.0 to 8,000.0 g/mol; (vii) a weight-average molecular weight (M_W) from 250,000.0 to 300,000.0 g/mol; (viii) a z-average molecular weight (M_Z) from 1,800,000.0 to 2,500,000.0 g/mol.

2. The bimodal ethylene-*co*-1-butene copolymer of claim 1 wherein the melt property space of the bimodal ethylene-*co*-1-butene copolymer is further defined by any one of limitations (i) to (~~viii~~iii): (i) a melt index I_2 from 0.005 to 0.10 g/10 min. measured according to ASTM D1238-13 (190° C., 2.16 kg, "I_2"); (ii) a melt index I_5 from 0.25 to 0.40 g/10 min. measured according to ASTM D1238-13 (190° C., 5.0 kg, "I_5"); and (iii) a melt flow ratio

I_{21}/I_2 (“MFR2”) from 100.0 to 150.0, wherein the I_{21} and I_2 values used to calculate the MFR2 are each in g/10 min. and are measured according to ASTM D1238-13 (190° C., 21.6 kg, “I_{21}”; and 190° C., 2.16 kg, “I_2”)~~; (iv) both (i) and (ii); (v) both (i) and (iii); (vi) both (ii) and (iii); and (vii) each of (i) to (iii)~~.

3. The bimodal ethylene-co-1-butene copolymer of claim 2 wherein the melt property space of the bimodal ethylene-co-1-butene copolymer is further defined by limitation (iv) both (i) and (ii).

4. The bimodal ethylene-co-1-butene copolymer of claim 2 wherein the melt property space of the bimodal ethylene-co-1-butene copolymer is further defined by limitation (v) both (i) and (iii).

5. The bimodal ethylene-co-1-butene copolymer of claim 2 wherein the melt property space of the bimodal ethylene-co-1-butene copolymer is further defined by limitation (vi) both (ii) and (iii).

6. The bimodal ethylene-co-1-butene copolymer of claim 2 wherein the melt property space of the bimodal ethylene-co-1-butene copolymer is further defined by limitation (vii) each of (i) to (iii).

~~3. The bimodal ethylene-*co*-1-butene copolymer of claim 1 or 2 characterized by any one of resin property limitations (i) to (xxxiii): (i) a density from 0.9410 to 0.9550 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13, Method B; (ii) a component fraction split characterized by a weight fraction of the HMW component from 50.0 to 60.0 wt%; and a weight fraction of the LMW component fraction is from 50.0 to 40.0 wt% of the combined weight of the HMW and LMW components, measured according to the Gel Permeation Chromatography (GPC) Test Method; (iii) a component molecular weight spread characterized by a ratio of the weight-average molecular weight of the HMW component ($M_{w\text{-}HMW}$) to the weight-average molecular weight of the LMW component ($M_{w\text{-}LMW}$) from 38.0 to 44.0, measured according to the GPC Test Method; (iv) a molecular mass dispersity (M_w/M_n), $Đ_M$, from 34 to 44, wherein M_w and M_n are measured according to the GPC Test Method; (v) the $M_{w\text{-}HMW}$ is from 435,000 to 465,000 g/mol measured according to the GPC Test Method; (vi) a number-average molecular weight (M_n) from 6,900.0 to 8,000.0 g/mol; (vii) a weight-average molecular weight (M_w) from 250,000.0 to 300,000.0 g/mol; (viii) a z-average molecular weight (M_z) from 1,800,000.0 to 2,500,000.0 g/mol; (ix) both (i) and (ii); (x) both (i) and (iii); (xi) both (i) and (iv); (xii) both (i) and (v); (xiii) both (i) and (vi); (xiv) both (i) and (vii); (xvi) both (i) and (viii); (xvii) both (ii) and (iii); (xviii) both (ii) and (iv); (xix) both (ii) and (v); (xx) both (ii) and (vi); (xxi) both (ii) and (vii); (xxii) both (ii) and (viii); (xxiii) both (iii)~~

~~and (iv); (xxiv) both (iii) and (v); (xxv) both (iii) and (vi); (xxvi) both (iii) and (vii); (xxvii) both (iii) and (viii); (xxviii) both (iv) and (v); (xxix) both (iv) and (vi); (xxx) both (iv) and (vii); (xxxi) both (iv) and (viii); (xxxii) any seven of (i) to (viii); and (xxxiii) each of (i) to (viii).~~

~~4~~7. The bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~3~~ 6 that, when characterized in the form of a blown film and having a thickness of 0.0127 millimeter is characterized by any one of limitations (i) to (~~xiii~~iv): (i) a dart impact from 271 to 401 grams (g) measured according to the Dart Impact Test Method; (ii) a gauge variation from 10.0% to 16% measured according to the Gauge Variation Test Method; (iii) a bubble stability rating, at maximum line speed (MLS) 76.2 meters per minute, of 3, 4, or 5 measured according to the Bubble Stability Test Method; (iv) an Elmendorf tear in cross direction (CD) from 60.0 to 190.0 gram-force (gf) and/or an Elmendorf tear in machine direction (MD) from 15 to 35 gf, measured according to the Elmendorf Tear Test Method~~; (v) both (i) and (ii); (vi) both (i) and (iii); (vii) both (i) and (iv); (viii) both (ii) and (iii); (ix) both (ii) and (iv); (x) both (iii) and (iv); (xi) any three of (i) to (iv); and (xii) each of (i) to (iv)~~.

8. The bimodal ethylene-co-1-butene copolymer of claim 7 that, when characterized in the form of a blown film and having a thickness of 0.0127 millimeter is characterized by limitation (v) both (i) and (ii).

9. The bimodal ethylene-co-1-butene copolymer of claim 7 that, when characterized in the form of a blown film and having a thickness of 0.0127 millimeter is characterized by limitation (xii) each of (i) to (iv).

~~5~~10. A method of synthesizing the bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~4~~9, the method consisting essentially of (a) copolymerizing ethylene (monomer) and 1-butene (comonomer) with a combination of a bimodal catalyst system and a trim catalyst in the presence of molecular hydrogen gas (H_2) and, optionally, an induced condensing agent (ICA) in one polymerization reactor (e.g., one fluidized bed, gas phase polymerization reactor (FB-GPP reactor)) under effective polymerizing conditions to give an initial bimodal ethylene-*co*-1-butene copolymer, (b) removing the initial bimodal ethylene-*co*-1-butene copolymer from the reactor (e.g., the FB-GPP reactor) to give a removed bimodal ethylene-*co*-1-butene copolymer, and (c) oxygen tailoring the removed bimodal ethylene-*co*-1-butene copolymer to give an oxygen-tailored bimodal ethylene-*co*-1-butene copolymer.

~~6~~11. The method of claim ~~5~~ 10 further consisting essentially of adding at least one additive to the oxygen-tailored bimodal ethylene-*co*-1-butene copolymer to give a formulation comprising the oxygen-tailored bimodal ethylene-*co*-1-butene copolymer and the at least one additive.

~~7~~12. A manufactured article comprising the bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~4~~9.

~~8~~13. A film consisting essentially of the bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~4~~ 9 and characterized when at a thickness of 0.013 millimeter or greater as having a dart impact of greater than 290 grams measured by the Dart Impact Test Method.

~~9~~14. A method of making a blown film, the method comprising extruding a melt of the bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~4~~ 9 through a die configured for forming a bubble so as to make a bubble of the bimodal ethylene-*co*-1-butene copolymer, and blowing (inflating) the bubble with a film-blowing machine, thereby making the blown film.

~~10~~15. A blown film made by the method of claim ~~9~~ 14 and consisting essentially of the bimodal ethylene-*co*-1-butene copolymer of any one of claims 1 to ~~4~~9.