POLYETHYLENE COPOLYMER RESINS AND FILMS

FIELD

[0001] Polyethylene copolymer, film, article, and methods.

INTRODUCTION

[0002] WO 2006/007046 A2 to John F. Szul, et al., relates to methods for producing polymers with control over composition distribution. WO 2006/138007 A1 to Rainer Kolb, et al., relates to single catalyst low, medium and high density polyethylenes. US 8,227,552 B2 and US 8,497,329 B2, both to Rainer Kolb, et al., relate to methods of controlling polymer properties. US 2016/0297907 A1 to Mark G. Goode, et al., relates to methods for controlling polymer properties. WO 2017/132092 A1 to Cliff R. Mure, et al., relates to a polyolefin film with improved toughness.

SUMMARY

[0003] We sought an ethylene/alpha-olefin copolymer that can be made into a blown film characterized by enhanced (increased) bubble stability, i.e., decreased bubble instability.

[0004] Our technical solution comprises an ethylene/alpha-olefin copolymer that can be synthesized in a fluidized-bed, gas phase polymerization (FB-GPP) reactor and made into a blown film. The ethylene/alpha-olefin copolymer is characterized by a bubble stability-effective combination of properties comprising density, melt flow ratio ("I_{21}/I_5"), and melt storage modulus G′ (G″=3,000 Pa). In one aspect, there is provided an ethylene/alpha-olefin copolymer characterized by a density from 0.947 to 0.949 gram per cubic centimeter (g/cm3), measured according to ASTM D792-13, Method B; a flow index ("I21") from 8.5 to 12.4 grams per 10 minutes (g/10 min.), measured according to ASTM D1238-13 (190° C., 21.6 kg); a melt flow ratio ("I21/I5") from 20.9 to 24.41 measured according to ASTM D1238-13 (190° C., 21.6 kg, "I21"; and 190° C., 5.0 kg, "I5"); and a melt storage modulus G′ (G″=3,000 Pa) value from 1950 to 2,155 Pascals (Pa) measured according to the Melt Storage Modulus Test Method of the description wherein melt storage G′ (G″=3,000 Pa) means melt storage modulus G′ measured at a dynamic frequency where loss modulus (G″) is equal to 3,000 Pascals. The synthesis in the FB-GPP reactor is characterized by a property-imparting-effective combination of operating conditions comprising reactor bed temperature and H2/C2 gas molar ratio. An example of the blown film consisting essentially of the ethylene/alpha-olefin copolymer is characterized by enhanced (increased) bubble stability, i.e., decreased bubble instability. The example of the film consisting essentially of the ethylene/alpha-olefin copolymer may be made or fabricated without internal bubble cooling (IBC) by any suitable method, including high stalk film blowing without IBC, and may optionally contain zero, one or more film additives. A

method of making the ethylene/alpha-olefin copolymer. A film comprising the ethylene/alpha-olefin copolymer. A method of making the film. A manufactured article comprising the film.

[0004a] In another aspect, there is provided a method of synthesizing the ethylene/alpha-olefin copolymer as defined herein, the method comprising contacting ethylene and the alpha-olefin with a reduced chromium oxide catalyst system in a fluidized bed, gas-phase polymerization (FB-GPP) reactor operating at a first reactor bed temperature (RBT1), a first average polymer residence time (avgPRT1), and a first ethylene partial pressure (C2P1) and receiving an ethylene (C2) feed, a comonomer (Cx) feed, a hydrogen (H2) feed, and, optionally, an oxygen (O2) feed wherein the feeds are characterized by a first H2/C2 gas molar ratio (H2/C2-1), a comonomer/ethylene gas molar ratio ("Cx/C2"), and a first O2/C2 gas volume ratio ("[O2/C2]1", vol/vol in ppmv); wherein RBT1 is from 104 to 108 degrees Celsius (° C.); avgPRT1 is from 1.70 to 3.10 hours, C2P1 is from 1,100 to 1,900 kilopascals (kPa); H2/C2-1 is from 0.01 to 0.10; Cx/C2 is from 0.0001 to 0.1; and O2/C2 is from 0.0000 to 0.163 volume/volume parts per million (ppmv); thereby synthesizing the ethylene/alpha-olefin copolymer in the FB-GPP reactor.

[0004b] In another aspect, there is provided a film comprising the ethylene/alpha-olefin copolymer as defined herein.

[0004c] In another aspect, there is provided a method of making the film as defined herein, the method comprising restricting in one dimension the ethylene/alpha-olefin copolymer, thereby giving the film.

[0004d] In another aspect, there is provided a manufactured article comprising the film as defined herein and a substance in need of covering, wherein the film is disposed to at least partially cover the substance.

[0004e] In another aspect, there is provided a film comprising an ethylene/alpha-olefin copolymer characterized by a density from 0.947 to 0.949 gram per cubic centimeter (g/cm3), measured according to ASTM D792-13, Method B; a flow index ("I21") from 8.5 to 12.4 grams per 10 minutes (g/10 min.), measured according to ASTM D1238-13 (190° C., 21.6 kg); a melt flow ratio ("I21/I5") from 20.5 to 24.4 measured according to ASTM D1238-13 (190° C., 21.6 kg, "I21"; and 190° C., 5.0 kg, "I5"); and a melt storage modulus G′ (G″=3,000 Pa) value from 1950 to 2,155 Pascals (Pa) measured according to the Melt Storage Modulus Test Method of the description wherein melt storage G′ (G″=3,000 Pa) means melt storage modulus G′ measured at a dynamic frequency where loss modulus (G″) is equal to 3,000 Pascals.

[0004f] In another aspect, there is provided a method of making the film as defined herein, the method comprising restricting in one dimension the ethylene/alpha-olefin copolymer, thereby giving the film.

[0004g] In another aspect, there is provided a manufactured article comprising the film as defined herein and a substance in need of covering, wherein the film is disposed to at least partially cover the substance.

DETAILED DESCRIPTION

[0005] The Summary and Abstract are incorporated here by reference.

[0006] Melt elasticity of a thermoplastic polymer can be thought of as the behavior of a melt of the polymer during a shaping process such as extrusion or film formation. It is one of the determinants of viscoelastic melt behavior, wherein viscosity decreases with increasing shear rate. Unsatisfactory melt elasticity may undesirably cause die swell during extrusion or problems with bubble stability during film blowing. A measure of, or proxy for, melt

CLAIMS

1. An ethylene/alpha-olefin copolymer characterized by a density from 0.947 to 0.949 gram per cubic centimeter (g/cm^3), measured according to ASTM D792-13, Method B; a flow index ("I_{21}") from 8.5 to 12.4 grams per 10 minutes (g/10 min.), measured according to ASTM D1238-13 (190° C., 21.6 kg); a melt flow ratio ("I_{21}/I_5") from 20.9 to 24.41 measured according to ASTM D1238-13 (190° C., 21.6 kg, "I_{21}"; and 190° C., 5.0 kg, "I_5"); and a melt storage modulus G′ (G″=3,000 Pa) value from 1950 to 2,155 Pascals (Pa) measured according to the Melt Storage Modulus Test Method of the description wherein melt storage G′ (G″=3,000 Pa) means melt storage modulus G′ measured at a dynamic frequency where loss modulus (G″) is equal to 3,000 Pascals.

2. The ethylene/alpha-olefin copolymer of claim 1 having any one of limitations (i) to (v): (i) flow index (I_{21}) from 8.8 to 12.3 g/10 min.; (ii) a melt flow ratio (I_{21}/I_5) from 21.0 to24.0; (iii) a weight average molecular weight (Mw) greater than 100,000 grams per mole (g/mol); (iv) a molecular mass dispersity (M_w/M_n), $Đ_M$, of greater than 25; and (v) melt storage modulus G′ (G″=3,000 Pa) from 2010 to 2,140 Pa.

3. The ethylene/alpha-olefin copolymer of claim 1 or 2 wherein the alpha-olefin is 1-butene or 1-hexene.

4. A method of synthesizing the ethylene/alpha-olefin copolymer of any one of claims 1 to 3, the method comprising contacting ethylene and the alpha-olefin with a reduced chromium oxide catalyst system in a fluidized bed, gas-phase polymerization (FB-GPP) reactor operating at a first reactor bed temperature (RBT1), a first average polymer residence time (avgPRT1), and a first ethylene partial pressure (C2P1) and receiving an ethylene (C2) feed, a comonomer (Cx) feed, a hydrogen (H_2) feed, and, optionally, an oxygen (O_2) feed wherein the feeds are characterized by a first H2/C2 gas molar ratio (H2/C2-1), a comonomer/ethylene gas molar ratio ("Cx/C2"), and a first O2/C2 gas volume ratio ("[O2/C2]1", vol/vol in ppmv); wherein RBT1 is from 104 to 108 degrees Celsius (° C.); avgPRT1 is from 1.70 to 3.10 hours, C2P1 is from 1,100 to 1,900 kilopascals (kPa); H2/C2-1 is from 0.01 to 0.10; Cx/C2 is from 0.0001 to 0.1; and O2/C2 is from 0.0000 to 0.163 volume/volume parts per million (ppmv); thereby synthesizing the ethylene/alpha-olefin copolymer in the FB-GPP reactor.

5. The method of claim 4 further comprising removing the ethylene/alpha-olefin copolymer from the FB-GPP reactor to give a removed ethylene/alpha-olefin copolymer.

6. A film comprising the ethylene/alpha-olefin copolymer of claim 1, 2 or 3.

7. A method of making the film of claim 6, the method comprising restricting in one dimension the ethylene/alpha-olefin copolymer, thereby giving the film.

8. A manufactured article comprising the film of claim 6 and a substance in need of covering, wherein the film is disposed to at least partially cover the substance.

9. A film comprising an ethylene/alpha-olefin copolymer characterized by a density from 0.947 to 0.949 gram per cubic centimeter (g/cm^3), measured according to ASTM D792-13, Method B; a flow index ("I_{21}") from 8.5 to 12.4 grams per 10 minutes (g/10 min.), measured according to ASTM D1238-13 (190° C., 21.6 kg); a melt flow ratio ("I_{21}/I_5") from 20.5 to 24.4 measured according to ASTM D1238-13 (190° C., 21.6 kg, "I_{21}"; and 190° C., 5.0 kg, "I_5"); and a melt storage modulus G′ (G″=3,000 Pa) value from 1950 to 2,155 Pascals (Pa) measured according to the Melt Storage Modulus Test Method of the description wherein melt storage G′ (G″=3,000 Pa) means melt storage modulus G′ measured at a dynamic frequency where loss modulus (G″) is equal to 3,000 Pascals.

10. The film of claim 9 wherein the ethylene/alpha-olefin copolymer has any one of limitations

(i) to (v): (i) flow index (I_{21}) from 8.8 to 12.3 g/10 min.; (ii) a melt flow ratio (I_{21}/I_5) from 21.0 to 24.0; (iii) a weight average molecular weight (Mw) greater than 100,000 grams per mole (g/mol); (iv) a molecular mass dispersity (M_w/M_n), $Đ_M$, of greater than 25; and (v) melt storage modulus G′ (G″=3,000 Pa) from 2010 to 2,140 Pa.

11. The film of claim 9 or 10 wherein the alpha-olefin is 1-butene or 1-hexene.

12. A method of making the film of claim 9, the method comprising restricting in one dimension the ethylene/alpha-olefin copolymer, thereby giving the film.

13. A manufactured article comprising the film of claim 9 and a substance in need of covering, wherein the film is disposed to at least partially cover the substance.