SELECTIVELY TRANSITIONING POLYMERIZATION PROCESSES

FIELD

[0001] Transitioning a polymerization process and use of a process control variable therefor.

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 recognized a need for substantially changing melt elasticity of an ethylene/alpha-olefin copolymer being made by catalyzed polymerization of ethylene and alpha-olefin in a single gas-phase polymerization (GPP) reactor without changing the alpha-olefin (comonomer) and without substantially changing the copolymer's density (ρ).

[0004] A technical solution to this problem was not obvious from the prior art because we recognized that the number of process control variables that are available to a skilled artisan in continuous polymerization processes in gas-phase polymerization reactor are limited, and it could not be predicted which, if any, of the process control variables could affect melt elasticity and, of those, which could do so without substantially changing density of the ethylene/alpha-olefin copolymer and without using a different comonomer or a second reactor or without substantially changing the polymerization catalyst.

[0005] Our technical solution includes a method of selectively transitioning a polymerization process making an ethylene/alpha-olefin copolymer via changing one or more process control variable(s) in such a way that melt elasticity of the copolymer is substantially changed without changing the comonomer and without substantially changing density (ρ) of the copolymer and without using a second reactor or substantially changing the polymerization catalyst.

[0005a] In one aspect, there is provided a method of transitioning a polymerization reaction making an ethylene/alpha-olefin copolymer with a same chromium-based catalyst system in a single gas-phase polymerization 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 expressed in parts per million by volume (ppmv)); the method comprising: (a) making, in the reactor under first polymerization conditions comprising H2/C2-1, Cx/C2, [O2/C2]1, RBT1, and C2P1, a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) value (MSM1) measured according to the Melt Storage Modulus Test Method of the description; wherein a melt storage modulus 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, a first Composition Distribution Breadth Index value (CDBI1), a first density (ρ1), and a first flow index ("(I_{21})1"); followed by (b1), (b2), or (b3): (b1) raising or lowering the reactor bed temperature in the gas-phase polymerization reactor from RBT1 to a second reactor bed temperature (RBT2), which is from 1 to 10 degrees Celsius (° C.) higher or lower than RBT1; or (b2) decreasing or increasing, respectively, the H2/C2 gas molar ratio of the hydrogen and ethylene feeds from H2/C2-1 to a second H2/C2 gas molar ratio (H2/C2-2), which is from 0.01 to 0.20 lower or higher than H2/C2-1, in such a way that the comonomer/ethylene gas molar ratio value Cx/C2 is unchanged; or (b3) decreasing or increasing the flow index of the ethylene/alpha-olefin copolymer from (I_{21})1 to a second flow index ("(I_{21})2"), which is from 0.1 to 5 grams per 10 minutes (g/10 min.) lower or higher than (I_{21})1; wherein steps (a) and any one of (b1) to (b3) are conducted at the same comonomer/ethylene gas molar ratio value Cx/C2; thereby substantially changing the melt storage modulus G′ (G″=3,000 Pa) of the ethylene/alpha-olefin copolymer without using a different alpha-olefin in the Cx feed and without substantially changing its density; wherein a substantial change in melt storage modulus G′ (G″=3,000 Pa) means the MSM2 of the second ethylene/alpha-olefin copolymer is higher or lower than the MSM1 of the first ethylene/alpha-olefin copolymer by at least 10.0%; and wherein without substantially changing density of the ethylene/alpha-olefin copolymer means ρ2 is within ±0.004 g/cm^3.

[0005b] Also, a method of compensating a transitioning polymerization process making an ethylene/alpha-olefin copolymer in such a way that in response to a change in reactor bed temperature a process control variable is inversely changed to offset the effect of the change in reactor bed temperature on melt elasticity of the ethylene/alpha-olefin copolymer such that the melt elasticity and ρ of the ethylene/alpha-olefin copolymer are substantially unchanged and without using a different comonomer or a second reactor or without substantially changing the polymerization catalyst.

[0005c] In another aspect, there is provided a method of compensating a transitioning polymerization reaction making an ethylene/alpha-olefin copolymer with a same chromium-based catalyst system in a single gas-phase polymerization 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); the method comprising: (a) making, in the reactor under first polymerization conditions comprising H2/C2-1, Cx/C2, [O2/C2]1, RBT1, and C2P1, a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) value (MSM1) measured according to the Melt Storage Modulus Test Method, a first Composition Distribution Breadth Index value (CDBI1), a first density (ρ1), and a first flow index ("(I_{21})1"); (b1) raising or lowering the reactor bed temperature in the gas-phase polymerization reactor from RBT1 to a second reactor bed temperature (RBT2), which is from 1° to 10° C. higher or lower than RBT1 and (c) decreasing or increasing, respectively, the H2/C2 gas molar ratio in such a way that the comonomer/ethylene gas molar ratio value Cx/C2 is unchanged, wherein steps (a) to (c) are done without changing the alpha-olefin of the Cx feed; thereby making at steady-state conditions after step (c) a second ethylene/alpha-olefin copolymer at a different reactor bed temperature (RBT2) than the first reactor bed temperature RBT1, wherein the second ethylene/alpha-olefin copolymer has the same alpha-olefin and has a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) and second density value (ρ2), wherein MSM2 is the same as MSM1 and ρ2 is the same as ρ1.

[0005d] Also, uses of the process control variable(s) therefor.

[0005e] In another aspect, there is provided use of reactor bed temperature, H2/C2 gas molar ratio, or flow index to transition a polymerization reaction using a same chromium-based catalyst system in a single gas-phase polymerization reactor from making a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) (MSM1) to making a second ethylene/alpha-olefin copolymer having a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) that is substantially different than MSM1 without changing the alpha-olefin composition and without substantially changing the ethylene/alpha-olefin copolymer's density; wherein melt storage modulus is measured according to the Melt Storage Modulus Test Method of the description; wherein melt storage modulus 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; wherein a substantial

change in melt storage modulus G′ (G″=3,000 Pa) means the MSM2 of the second ethylene/alpha-olefin copolymer is higher or lower than the MSM1 of the first ethylene/alpha-olefin copolymer by at least 10.0%; and wherein without substantially changing density of the ethylene/alpha-olefin copolymer means ρ2 is within ±0.004 g/cm^3.

CLAIMS

1. A method of transitioning a polymerization reaction making an ethylene/alpha-olefin copolymer with a same chromium-based catalyst system in a single gas-phase polymerization 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 expressed in parts per million by volume (ppmv)); the method comprising: (a) making, in the reactor under first polymerization conditions comprising H2/C2-1, Cx/C2, [O2/C2]1, RBT1, and C2P1, a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) value (MSM1) measured according to the Melt Storage Modulus Test Method of the description; wherein a melt storage modulus 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, a first Composition Distribution Breadth Index value (CDBI1), a first density (ρ1), and a first flow index ("(I_{21})1"); followed by (b1), (b2), or (b3): (b1) raising or lowering the reactor bed temperature in the gas-phase polymerization reactor from RBT1 to a second reactor bed temperature (RBT2), which is from 1 to 10 degrees Celsius (° C.) higher or lower than RBT1; or (b2) decreasing or increasing, respectively, the H2/C2 gas molar ratio of the hydrogen and ethylene feeds from H2/C2-1 to a second H2/C2 gas molar ratio (H2/C2-2), which is from 0.01 to 0.20 lower or higher than H2/C2-1, in such a way that the comonomer/ethylene gas molar ratio value Cx/C2 is unchanged; or (b3) decreasing or increasing the flow index of the ethylene/alpha-olefin copolymer from (I_{21})1 to a second flow index ("(I_{21})2"), which is from 0.1 to 5 grams per 10 minutes (g/10 min.) lower or higher than (I_{21})1; wherein steps (a) and any one of (b1) to (b3) are conducted at the same comonomer/ethylene gas molar ratio value Cx/C2; thereby substantially changing the melt storage modulus G′ (G″=3,000 Pa) of the ethylene/alpha-olefin copolymer without using a different alpha-olefin in the Cx feed and without substantially changing its density;

wherein a substantial change in melt storage modulus G′ (G″=3,000 Pa) means the MSM2 of the second ethylene/alpha-olefin copolymer is higher or lower than the MSM1 of the first ethylene/alpha-olefin copolymer by at least 10.0%; and

wherein without substantially changing density of the ethylene/alpha-olefin copolymer means ρ2 is within ±0.004 g/cm^3.

2. The method of claim 1 comprising steps (a) and (b1) and any one of limitations (i) to (iii): (i) wherein in step (b1) the reactor bed temperature RBT1 is increased or decreased to the reactor bed temperature RBT2 and wherein RBT2 is from 1° to 5° C. higher or lower, respectively than RBT1; (ii) wherein the second ethylene/alpha-olefin copolymer has a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) of from 500 to 5,000 Pascals (Pa), wherein MSM2 is substantially different than MSM1; and (iii) both (i) and (ii).

3. The method of claim 1 comprising steps (a) and (b2) and any one of limitations (i) to (iii): (i) wherein in step (b2) the H2/C2 gas molar ratio of the hydrogen and ethylene feeds is decreased or increased, respectively, from H2/C2-1 to a second H2/C2 gas molar ratio (H2/C2-2) and wherein H2/C2-2 is from 0.01 to 0.20 lower or higher, respectively, than H2/C2-1; (ii) wherein the second ethylene/alpha-olefin copolymer has a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) of from 500 to 5,000 Pascals (Pa), wherein MSM2 is substantially different than MSM1; and (iii) both (i) and (ii).

4. The method of claim 1 comprising steps (a) and (b3) and any one of limitations (i) to (iii): (i) wherein in step (b3) the flow index (I_{21})1 of the first ethylene/alpha-olefin copolymer is increased or decreased to a second flow index (“(I_{21})2”) of the second ethylene/alpha-olefin copolymer, wherein (I_{21})1 is from 0.1 to 5 g/10 min. higher or lower, respectively, than (I_{21})2; (ii) wherein the second ethylene/alpha-olefin copolymer has a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) of from 500 to 5,000 Pascals (Pa), wherein MSM2 is substantially different than MSM1; and (iii) both (i) and (ii).

5. A method of compensating a transitioning polymerization reaction making an ethylene/alpha-olefin copolymer with a same chromium-based catalyst system in a single gas-phase polymerization 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); the method comprising: (a) making, in the reactor under first polymerization conditions comprising H2/C2-1, Cx/C2, [O2/C2]1, RBT1, and C2P1, a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) value (MSM1) measured according to the Melt Storage Modulus Test Method, a first Composition Distribution Breadth Index value (CDBI1), a first density (ρ1), and a first flow index (“(I_{21})1”); (b1) raising or lowering the reactor bed temperature in the gas-phase polymerization reactor from RBT1 to a second reactor bed

temperature (RBT2), which is from 1° to 10° C. higher or lower than RBT1 and (c) decreasing or increasing, respectively, the H2/C2 gas molar ratio in such a way that the comonomer/ethylene gas molar ratio value Cx/C2 is unchanged, wherein steps (a) to (c) are done without changing the alpha-olefin of the Cx feed; thereby making at steady-state conditions after step (c) a second ethylene/alpha-olefin copolymer at a different reactor bed temperature (RBT2) than the first reactor bed temperature RBT1, wherein the second ethylene/alpha-olefin copolymer has the same alpha-olefin and has a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) and second density value (ρ2), wherein MSM2 is the same as MSM1 and ρ2 is the same as ρ1.

6. The method of claim 5 having any one of limitations (i) to (v): (i) wherein in step (b1) the reactor bed temperature RBT1 is increased to the reactor bed temperature RBT2 and wherein RBT2 is from 1° to 5° C. higher than RBT1; and wherein in step (c) the H2/C2 gas molar ratio of the hydrogen and ethylene feeds is decreased from H2/C2-1 to a second H2/C2 gas molar ratio (H2/C2-2) and wherein H2/C2-2 is from 0.01 to 0.20 lower than H2/C2-1; (ii) wherein melt storage modulus G′ (G″=3,000 Pa) (MSM2) for the second ethylene/alpha-olefin copolymer is from 500 to 5,000 Pascals (Pa); (iii) both (i) and (ii); (iv) wherein in step (b1) the reactor bed temperature RBT1 is decreased to the reactor bed temperature RBT2 and wherein RBT2 is from 1° to 5° C. lower than RBT1; and wherein in step (c) the H2/C2 gas molar ratio of the hydrogen and ethylene feeds is increased from H2/C2-1 to a second H2/C2 gas molar ratio (H2/C2-2) and wherein H2/C2-2 is from 0.01 to 0.20 higher than H2/C2-1; and (v) both (ii) and (iv).

7. The method of any one of claims 1 to 6 wherein the Composition Distribution Breadth Index value (CDBI2) and density (ρ2) of the second ethylene/alpha-olefin copolymer is substantially unchanged from the Composition Distribution Breadth Index value (CDBI1) and density (ρ1), respectively, of the first ethylene/alpha-olefin copolymer; wherein without substantially changing CDBI value of the ethylene/alpha-olefin copolymer means the CDBI2 value is within plus-or-minus (±) 10.0% of the CDBI1 value.

8. Use of reactor bed temperature, H2/C2 gas molar ratio, or flow index to transition a polymerization reaction using a same chromium-based catalyst system in a single gas-phase polymerization reactor from making a first ethylene/alpha-olefin copolymer having a first melt storage modulus G′ (G″=3,000 Pa) (MSM1) to making a second ethylene/alpha-olefin copolymer having a second melt storage modulus G′ (G″=3,000 Pa) (MSM2) that is substantially different than MSM1 without changing the alpha-olefin composition and without substantially changing the ethylene/alpha-olefin copolymer's density;

wherein melt storage modulus is measured according to the Melt Storage Modulus Test Method of the description; wherein melt storage modulus 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;

wherein a substantial change in melt storage modulus G′ (G″=3,000 Pa) means the MSM2 of the second ethylene/alpha-olefin copolymer is higher or lower than the MSM1 of the first ethylene/alpha-olefin copolymer by at least 10.0%; and

wherein without substantially changing density of the ethylene/alpha-olefin copolymer means ρ2 is within ±0.004 g/cm^3.

9. The use of claim 8 further using a change in H2/C2 gas molar ratio to offset the change in reactor bed temperature in order to compensate the transitioning polymerization reaction by changing the melt storage modulus G′ (G″=3,000 Pa) of the second ethylene/alpha-olefin copolymer from MSM2 to MSM1.