BIMODAL POLY(ETHYLENE-*CO*-1-ALKENE) COPOLYMER

FIELD

[0001] Bimodal poly(ethylene-*co*-1-alkene) copolymer and related methods and articles.

INTRODUCTION

[0002] Patent application publications and patents in or about the field include US7868092B2, US9169337B2, WO2008147968, and USSN 62/712,527 filed July 31, 2018.

SUMMARY

[0003] We discovered a bimodal poly(ethylene-*co*-1-alkene) copolymer. The copolymer comprises a higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and a lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component). The copolymer is characterized by a unique combination of features comprising, or indicated by, its density; molecular weight distributions; component weight fraction amount; and viscoelastic properties; and at least one of environmental stress-cracking resistance and resin swell.

[0003a] In one aspect, there is provided a bimodal poly(ethylene-*co*-1-alkene) copolymer comprising a higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and a lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component), the copolymer being characterized by a combination of features comprising each of features (a) to (e) and features (f1) and (g): (a) a density greater than 0.955 gram per cubic centimeter (g/cm_3) measured according to ASTM D792-13 (Method B, 2-propanol); (b) a first molecular weight distribution that is a ratio of M_w/M_n from 13 to 25, wherein M_w is weight-average molecular weight and M_n is number-average molecular weight, both measured by Gel Permeation Chromatography (GPC); (c) a second molecular weight distribution that is a ratio of M_z/M_w greater than 8, wherein M_z is z-average molecular weight and M_w is weight-average molecular weight, both measured by GPC; (d) a component weight fraction amount wherein the HMW copolymer component is less than 28 weight percent (wt%) of the combined weight of the HMW and LMW copolymer components; and (e) a high load melt index (HLMI or I_{21}) from 20 to 45 grams per 10 minutes (g/10 min.) measured according to ASTM D1238-13 (190° C., 21.6 kg); and (f1) an environmental stress-cracking resistance (ESCR) (10% Igepal, F50) of from 150 hours to 500 hours, measured according to ASTM D1693-15, Method B; and (g) a resin swell t1000 of greater than 7.7 seconds, measured according to the Resin Swell t1000 Test Method.

[0003b] In another aspect, there is provided a bimodal poly(ethylene-*co*-1-alkene) copolymer comprising a higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and a lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component), the copolymer being characterized by a combination of features comprising each of features (a) to (e) and feature (f2) and, optionally feature (g): (a) a density greater than 0.955 gram per cubic centimeter (g/cm_3) measured according to ASTM D792-13 (Method B, 2-propanol); (b) a first molecular weight distribution that is a ratio of M_w/M_n from 13 to 25, wherein M_w is weight-average molecular weight and M_n is number-average molecular weight, both measured by Gel Permeation Chromatography (GPC); (c) a second molecular weight distribution that is a ratio of M_z/M_w greater than 8, wherein M_z is z-average molecular weight and M_w is weight-average molecular weight, both measured by GPC; (d) a component weight fraction amount wherein the HMW copolymer component is less than 28 weight percent (wt%) of the combined weight of the HMW and LMW copolymer components; and (e) a high load melt index (HLMI or I_{21}) from 20 to 45 grams per 10 minutes (g/10 min.) measured according to ASTM D1238-13 (190° C., 21.6 kg); and (f2) an environmental stress-cracking resistance in hours as a function of melt flow ratio, wherein the function is defined by Equation 1: ESCR (10% Igepal, F50) > (10 * MFR5 * 1 hour) – 150 hours (Eq. 1), wherein > means greater than; * means multiplication; ESCR (10% Igepal, F50) is the number of hours to failure measured according to ASTM D1693-15, Method B; and MFR5 is a ratio of the (e) HLMI divided by a melt index I_5 expressed in g/10 min. measured according to ASTM D1238-13 (190° C., 5.0 kg); and, optionally (g) a resin swell t1000 of greater than 7.7 seconds, measured according to the Resin Swell t1000 Test Method.

[0003c] The disclosure also relates to ~~Additional inventive embodiments include~~ a method of making the copolymer, a formulation comprising the copolymer and at least one additive that is different than the copolymer, a method of making a manufactured article from the copolymer or formulation; the manufactured article made thereby, and use of the manufactured article.

[0003d] In another aspect, there is provided a method of making the bimodal poly(ethylene-*co*-1-alkene) copolymer as defined herein, the method comprising contacting ethylene and 1-alkene with a bimodal catalyst system in a single polymerization reactor under effective polymerization conditions to give the bimodal poly(ethylene-*co*-1-alkene) copolymer; wherein the bimodal catalyst system consists essentially of a metallocene catalyst, a single-site non-metallocene catalyst that is a bis((alkyl-substituted phenylamido)ethyl)amine catalyst, optionally a host material, and optionally an activator; wherein the host material, when present, is selected from at least one of an inert hydrocarbon liquid and a solid support; wherein the metallocene catalyst is an activation reaction product of contacting an activator with a metal-ligand complex of formula

$(R_{1-2}Cp)((alkyl)_{1-3}Indenyl)MX_2$, wherein R is hydrogen, methyl, or ethyl; each alkyl independently is a (C_1-C_4)alkyl; M is titanium, zirconium, or hafnium; and each X is independently a halide, a $(C_1$ to $C_{20})$alkyl, a $(C_7$ to $C_{20})$aralkyl, a $(C_1$ to $C_6)$alkyl-substituted $(C_6$ to $C_{12})$aryl, or a $(C_1$ to $C_6)$alkyl-substituted benzyl; and wherein the bis((alkyl-substituted phenylamido)ethyl)amine catalyst is an activation reaction product of contacting an activator with a bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2, wherein each R^1 is independently selected from F, Cl, Br, I, benzyl, $-CH_2Si(CH_3)_3$, a (C_1-C_5)alkyl, and a (C_2-C_5)alkenyl.

[0003e] In another aspect, there is provided a formulation comprising the bimodal poly(ethylene-*co*-1-alkene) copolymer as defined herein and at least one additive that is different than the copolymer.

[0003f] In another aspect, there is provided a method of making a manufactured article, the method comprising extruding-melt-blowing the bimodal poly(ethylene-*co*-1-alkene) copolymer as defined herein, or the formulation as defined herein, under effective conditions so as to make the manufactured article.

[0003g] In another aspect, there is provided the manufactured article made by the method as defined herein.

[0003h] In another aspect, there is provided use of the manufactured article as defined herein in storing or transporting a material in need of storing or transporting.

DETAILED DESCRIPTION

[0004] The bimodal poly(ethylene-*co*-1-alkene) copolymer is a composition of matter. The bimodal poly(ethylene-*co*-1-alkene) copolymer comprises the higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and the lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component). The copolymer is characterized by the unique combination of features comprising, or indicated by, its density; molecular weight distributions; component weight fraction amount; and viscoelastic properties; and at least one, alternatively each of environmental stress-cracking resistance and resin swell. Embodiments of the copolymer may be characterized by refined or additional features and/or by features of one or both of its HMW and LMW copolymer components. The copolymer is a so-called reactor copolymer because it is made in a single polymerization reactor using a bimodal catalyst system effective for simultaneously making the HMW and LMW copolymer components *in situ*. The same copolymer composition cannot be made by separately making the HMW copolymer component and separately making the LMW copolymer component, and then blending the separately made components together.

CLAIMS

1. A bimodal poly(ethylene-*co*-1-alkene) copolymer comprising a higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and a lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component), the copolymer being characterized by a combination of features comprising each of features (a) to (e) and features (f1) and (g): (a) a density greater than 0.955 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13 (Method B, 2-propanol); (b) a first molecular weight distribution that is a ratio of M_W/M_n from 13 to 25, wherein M_W is weight-average molecular weight and M_n is number-average molecular weight, both measured by Gel Permeation Chromatography (GPC); (c) a second molecular weight distribution that is a ratio of M_Z/M_W greater than 8, wherein M_Z is z-average molecular weight and M_W is weight-average molecular weight, both measured by GPC; (d) a component weight fraction amount wherein the HMW copolymer component is less than 28 weight percent (wt%) of the combined weight of the HMW and LMW copolymer components; and (e) a high load melt index (HLMI or I_{21}) from 20 to 45 grams per 10 minutes (g/10 min.) measured according to ASTM D1238-13 (190° C., 21.6 kg); and (f1) an environmental stress-cracking resistance (ESCR) (10% Igepal, F50) of ~~greater than or equal to~~ from 150 hours to 500 hours, measured according to ASTM D1693-15, Method B; and (g) a resin swell t1000 of greater than 7.7 seconds, measured according to the Resin Swell t1000 Test Method.

2. A bimodal poly(ethylene-*co*-1-alkene) copolymer comprising a higher molecular weight poly(ethylene-*co*-1-alkene) copolymer component (HMW copolymer component) and a lower molecular weight poly(ethylene-*co*-1-alkene) copolymer component (LMW copolymer component), the copolymer being characterized by a combination of features comprising each of features (a) to (e) and feature (f2) and, optionally feature (g): (a) a density greater than 0.955 gram per cubic centimeter (g/cm^3) measured according to ASTM D792-13 (Method B, 2-propanol); (b) a first molecular weight distribution that is a ratio of M_W/M_n from 13 to 25, wherein M_W is weight-average molecular weight and M_n is number-average molecular weight, both measured by Gel Permeation Chromatography (GPC); (c) a second molecular weight distribution that is a ratio of M_Z/M_W greater than 8, wherein M_Z is z-average molecular weight and M_W is weight-average molecular weight, both measured by GPC; (d) a component weight fraction amount wherein the HMW copolymer component is less than 28 weight percent (wt%) of the combined weight of the HMW and LMW copolymer components; and (e) a high load melt index

(HLMI or I_{21}) from 20 to 45 grams per 10 minutes (g/10 min.) measured according to ASTM D1238-13 (190° C., 21.6 kg); and (f2) an environmental stress-cracking resistance in hours as a function of melt flow ratio, wherein the function is defined by Equation 1: ESCR (10% Igepal, F50) > (10 * MFR5 * 1 hour) – 150 hours (Eq. 1), wherein > means greater than; * means multiplication; ESCR (10% Igepal, F50) is the number of hours to failure measured according to ASTM D1693-15, Method B; and MFR5 is a ratio of the (e) HLMI divided by a melt index I_5 expressed in g/10 min. measured according to ASTM D1238-13 (190° C., 5.0 kg); and, optionally (g) a resin swell t1000 of greater than 7.7 seconds, measured according to the Resin Swell t1000 Test Method.

3. The bimodal poly(ethylene-*co*-1-alkene) copolymer of claim 1 or 2 further characterized by any one of refined features (a) to (e), ~~(f1) or~~ (f2), respectively, and (g): (a) the density is from 0.956 to 0.962 g/cm^3; (b) the M_W/M_n is from 14 to 21; (c) the M_Z/M_W is from 11 to 15; (d) the HMW copolymer component weight fraction amount is from 17 to 27 wt%; (e) the HLMI is from 25 to 41; ~~(f1) an ESCR (10% Igepal, F50) of from 150 to 500 hours or~~ (f2) the ESCR (10% Igepal, F50) is a function of the MFR5 as defined by Equation 1a: ESCR (10% Igepal, F50) > (10 * MFR5 * 1 hour) – 100 hours (Eq. 1a); and (g) the resin swell t1000 is from greater than 7.7 to 9.0 seconds.

4. The bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 3 further characterized by any one of features (h) to (~~q~~m): (h) M_W from 280,000 to 360,000 grams per mole (g/mol); (i) M_n from 15,000 to 23,000 grams g/mol; (j) M_Z from 3,000,000 to 4,800,000 g/mol; (k) an MFR5 from 16 to 27;~~(l) feature (g) in combination with (f1);~~ (~~m~~l) a melt index I_5 from 0.5 to 2.0 g/10 minutes; ~~(n) feature (g) in combination with feature (f2);~~ (~~o~~m) feature (g) in combination with feature (f1) and (f2), respectively~~; (p) a combination of any seven of features (h) to (o); and (q) a combination of each of features (h) to (o)~~.

5. The bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 4 further characterized by any one of features (~~r~~n) to (~~w~~s): (~~r~~n) the LMW copolymer component has a M_W from 45,000 to 55,000 g/mol; (~~s~~o) the LMW copolymer component has a M_n from 13,000 to 20,000 g/mol; (~~t~~p) the LMW copolymer component has a M_Z from 85,000 to 115,000 g/mol; (~~u~~q) the LMW copolymer component has a M_W/M_n ratio from 2.5 to 3.3; (~~v~~r) any three of features (~~r~~n) to (~~u~~q); (~~w~~s) each of features (~~r~~n) to (q~~u~~).

6. The bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 5 further characterized by any one of features (~~x~~t) to (~~a~~c~~y~~): (~~x~~t) the HMW copolymer component has a M_W

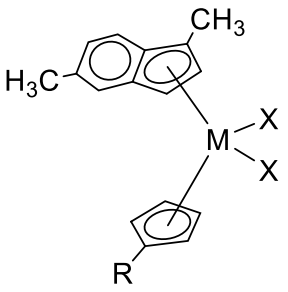
from 1,000,000 to 1,400,000 g/mol; (~~y~~u) the HMW copolymer component has a M_n from 220,000 to 320,000 g/mol; (~~z~~v) the HMW copolymer component has a M_z from 2,000,000 to 4,700,000 g/mol; (~~aa~~w) the HMW copolymer component has a M_w/M_n ratio from 4.0 to 4.4; (~~ab~~x) any three of features (~~x~~t) to (~~aa~~w); and (~~ac~~y) each of features (~~x~~t) to (~~aa~~w).

7. The bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 6 further characterized by feature (~~ad~~z) a melt strength of greater than 7.0 centinewtons (cN).

8. The bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 7 wherein the 1-alkene is 1-hexene and the bimodal poly(ethylene-*co*-1-alkene) copolymer is bimodal poly(ethylene-*co*-1-hexene) copolymer

9. A method of making the bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 8, the method comprising contacting ethylene and 1-alkene with a bimodal catalyst system in a single polymerization reactor under effective polymerization conditions to give the bimodal poly(ethylene-*co*-1-alkene) copolymer; wherein the bimodal catalyst system consists essentially of a metallocene catalyst, a single-site non-metallocene catalyst that is a bis((alkyl-substituted phenylamido)ethyl)amine catalyst, optionally a host material, and optionally an activator; wherein the host material, when present, is selected from at least one of an inert hydrocarbon liquid and a solid support; wherein the metallocene catalyst is an activation reaction product of contacting an activator with a metal-ligand complex of formula $(R_{1\text{-}2}Cp)((alkyl)_{1\text{-}3}Indenyl)MX_2$, wherein R is hydrogen, methyl, or ethyl; each alkyl independently is a $(C_1\text{-}C_4)$alkyl; M is titanium, zirconium, or hafnium; and each X is independently a halide, a $(C_1$ to $C_{20})$alkyl, a $(C_7$ to $C_{20})$aralkyl, a $(C_1$ to $C_6)$alkyl-substituted $(C_6$ to $C_{12})$aryl, or a $(C_1$ to $C_6)$alkyl-substituted benzyl; and wherein the bis((alkyl-substituted phenylamido)ethyl)amine catalyst is an activation reaction product of contacting an activator with a bis((alkyl-substituted phenylamido)ethyl)amine ZrR^1_2, wherein each R^1 is independently selected from F, Cl, Br, I, benzyl, $-CH_2Si(CH_3)_3$, a $(C_1\text{-}C_5)$alkyl, and a $(C_2\text{-}C_5)$alkenyl.

10. The method of claim 9 having at least one of the following features: the single polymerization reactor is a single gas phase polymerization reactor; and the metal-ligand complex is of formula (I):



(I)

, wherein R, M, and X are as defined therein.

11. A formulation comprising the bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 8 and at least one additive that is different than the copolymer.

12. A method of making a manufactured article, the method comprising extruding-melt-blowing the bimodal poly(ethylene-*co*-1-alkene) copolymer of any one of claims 1 to 8, or the formulation of claim 11, under effective conditions so as to make the manufactured article.

13. The manufactured article made by the method of claim 12.

14. Use of the manufactured article of claim 13 in storing or transporting a material in need of storing or transporting.