[0004] The composition distribution of an ethylene alpha-olefin copolymer refers to the distribution of comonomer, which form short chain branches, among the molecules that comprise the polyethylene polymer. When the amount of short chain branches varies among the polyethylene molecules, the resin is said to have a "broad" composition distribution. When the amount of comonomer per 1000 carbons is similar among the polyethylene molecules of different chain lengths, the composition distribution is said to be "narrow".

[0005] The composition distribution is known to influence the properties of copolymers, for example, stiffness, toughness, extracTable content, environmental stress crack resistance, and heat sealing, among other properties. The composition distribution of a polyolefin may be readily measured by methods known in the art, for example, Temperature Raising Elution Fractionation (TREF) or Crystallization Analysis Fractionation (CRYSTAF).

[0006] It is generally known in the art that a polyolefin's composition distribution is largely dictated by the type of catalyst used and is typically invariable for a given catalyst system. Ziegler-Natta catalysts and chromium based catalysts produce resins with broad composition distributions (BCD), whereas metallocene catalysts normally produce resins with narrow composition distributions (NCD).

[0007] Resins having a broad orthogonal composition distribution (BOCD) in which the comonomer is incorporated predominantly in the high molecular weight chains can lead to improved physical properties, for example toughness properties and environmental stress crack resistance (ESCR). Because of the improved physical properties of resins with orthogonal composition distributions needed for commercially desirable products, there exists a need for controlled techniques for forming polyethylene copolymers having a broad orthogonal composition distribution.

SUMMARY

[0008] An example described herein provides a method of selecting catalysts for making a product specific polyolefin using a blend polydispersity index (bPDI) map. The method includes generating a number of polymers for at least two catalysts, wherein each polymer is generated at a different hydrogen to ethylene ratio. One of the catalysts generates a higher molecular weight (hmw) polymer and another of the at least two catalysts generates a lower molecular weight (lmw) polymer. The weight averaged molecular weight and PDI is measured for each polymer. The relationship between the molecular weight of the polymers generated by each of the at least two catalysts and the ratio of hydrogen to ethylene is generated. A family of bPDI curves for polymers that would be made using a number of ratios of a blend of

the at least two catalysts for each of a number of ratios of hydrogen to ethylene is generated. A ratio for a blend of the catalysts is selected that generates a polymer having a bPDI that matches a polymer fabrication process. The ratio of the catalysts is confirmed by generating a polymer at each of the number of ratios of hydrogen to ethylene.

[0009] Another example provides a method of making a product specific polyolefin. The method includes selecting a catalyst blend based, at least in part, on a polydispersity index (PDI) map. The polydispersity map is generated by generating a number of polymers for at least two catalysts, wherein each polymer is generated at a different hydrogen to ethylene ratio. At least one of the catalysts generates a higher molecular weight polymer and another of the catalysts generates a lower molecular weight polymer. The molecular weight is measured for each polymer. The relationship between the molecular weight of the polymers generated by each of the at least two catalysts and the ratio of hydrogen to ethylene is determined. A family of bPDI curves for polymers that would be made using a number of ratios of a blend of the catalysts for each of a number of ratios of hydrogen to ethylene is generated. A ratio for the catalyst blend of the at least two catalysts that generates a polymer having a bPDI that matches a polymer fabrication process is selected. The product specific polyolefin is generated using the catalyst blend.

[0010] Another example provides a polymerization catalyst for forming a polyethylene copolymer. The polymerization catalyst includes a catalyst support and a blend of at least two catalysts. The catalysts are selected by generating a number of polymers for the catalysts, wherein each polymer is generated at a different hydrogen to ethylene ratio. One of the catalysts generates a polymer with a higher weight average molecular weight (hmw) and another of the catalysts generates a polymer with a lower weight average molecular weight (lmw). The ratio of hmw to lmw is greater than about 5.0 at a weight average molecular weight of between about 30,000 and about 150,000. The molecular weight is measured for each polymer and the relationship between the molecular weight of the polymers generated by each of the at least two catalysts and the ratio of hydrogen to ethylene is determined. A family of bPDI curves for polymers that would be made using a number of ratios of a blend of the catalysts for each of a number of ratios of hydrogen to ethylene is generated. A ratio for the catalyst blend of the catalysts that generates a polymer having a bPDI that matches a polymer fabrication process is selected.

[0011] Another example provides a polymerization catalyst for forming a polyethylene copolymer. The polymerization catalyst includes a catalyst support and a first catalyst that is impregnated on the catalyst support, wherein the first catalyst generates polymers

having a slope for a plot of H_2/C_2 versus 1/Mw of between about $1.0x10^{-6}$ and about $1.5\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between about 0.008 and about 0.012. The first catalyst generates a polymer having an MI of about 1.0 dg/10 min, a density of about 0.92 g/cc, and an melt index ratio (MIR) less than about 25. A second catalyst is impregnated on the catalyst support with the first catalyst, wherein the second catalyst generates polymers having a slope for a plot of H_2/C_2 versus 1/Mw of between about $3.0x10^{-6}$ and about $4\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between about 0.03 and about 0.04, the second catalyst generates a polymer having an MI of about 1.0 dg/10 min, a density of about 0.92 g/cc, and an melt index ratio (MIR) less than about 25.

[0011a] In one aspect, the present disclosure refers to a polymerization catalyst for forming a polyethylene copolymer, comprising: a catalyst support; a first catalyst that is impregnated on the catalyst support, wherein the first catalyst generates polymers having a slope for a plot of H_2/C_2 versus 1/Mw of between $1.0x10^{-6}$ and $1.5\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between 0.008 and 0.012, the first catalyst generates a polymer having a MI of 1.0 dg/10 min, a density of 0.92 g/cc, and a melt index ratio (MIR) less than 25, wherein the first catalyst impregnated on the catalyst support is bis(n-propylcyclopentadienyl) hafnium $(CH_3)_2$, bis(n-propylcyclopentadienyl) hafnium F_2, bis(n-propylcyclopentadienyl) hafnium Cl_2, or any combinations thereof; and a second catalyst that is impregnated on the catalyst support with the first catalyst, wherein the second catalyst generates polymers having a slope for a plot of H_2/C_2 versus 1/Mw of between $3.0x10^{-6}$ and $4\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between 0.03 and 0.04, the second catalyst generates a polymer having a MI of 1.0 dg/10 min, a density of 0.92 g/cc, and a melt index ratio (MIR) less than 25, wherein the second catalyst impregnated on the catalyst support is bis(1-ethylindenyl) zirconium $(CH_3)_2$, bis(1-ethylindenyl) zirconium F_2, bis(1-ethylindenyl) zirconium Cl_2, or any combinations thereof; wherein the ratio of H_2/C_2 is in ppm/mol%, and wherein the Mw is in g/mol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a schematic of a gas-phase reactor system, showing the addition of at least two catalysts, at least one of which is added as a trim catalyst.

[0013] Fig. 2 is a plot of a series of polymers that were prepared to test the relative abilities of a series of metallocene catalysts to prepare a resin having about a 1 melt index (MI) and a density (D) of about 0.92.

[0014] Fig. 3 is a plot of the series of polymers of Fig. 2, showing the melt index ratio (MIR) of the series of polymers made by different metallocene (MCN) catalysts.

[0015] Fig. 4 is a flow chart of a method for making a co-supported polymerization catalyst.

[0016] Figs. 5A, 5B, and 5C are log plots of the inverse of the molecular weight to the H_2/C_2 ratio for each of the hypothetical combinations.

[0017] Figs. 6A, 6B, and 6C are plots of the hydrogen response for each of the catalysts.

[0018] Figs. 7A, 7B, and 7C are bPDI maps generated for polymers produced by the catalyst blend.

[0019] Fig. 8 is a process flow diagram of a method for using a bPDI map to assist in forming a polymer.

[0020] Fig. 9 is a process flow diagram of a method 900 for selecting a catalyst blend, e.g., at block 802 of Fig. 8.

DETAILED DESCRIPTION

[0021] It has been discovered that when a support is impregnated with multiple catalysts, new polymeric materials with an improved balance of stiffness, toughness and processibility can be achieved, *e.g.*, by controlling the amounts and types of catalysts present on the support. As described in embodiments herein, an appropriate selection of the catalysts and ratios may be

CLAIMS

What is claimed is:

1. A polymerization catalyst for forming a polyethylene copolymer, comprising:

a catalyst support;

a first catalyst that is impregnated on the catalyst support, wherein the first catalyst generates polymers having a slope for a plot of H_2/C_2 versus 1/Mw of between $1.0x10^{-6}$ and $1.5\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between 0.008 and 0.012, the first catalyst generates a polymer having a MI of 1.0 dg/10 min, a density of 0.92 g/cc, and a melt index ratio (MIR) less than 25, wherein the first catalyst impregnated on the catalyst support is bis(n-propylcyclopentadienyl) hafnium $(CH_3)_2$, bis(n-propylcyclopentadienyl) hafnium F_2, bis(n-propylcyclopentadienyl) hafnium Cl_2, or any combinations thereof; and

a second catalyst that is impregnated on the catalyst support with the first catalyst, wherein the second catalyst generates polymers having a slope for a plot of H_2/C_2 versus 1/Mw of between $3.0x10^{-6}$ and $4\ x10^{-6}$, and wherein at a C_6/C_2 ratio of between 0.03 and 0.04, the second catalyst generates a polymer having a MI of 1.0 dg/10 min, a density of 0.92 g/cc, and a melt index ratio (MIR) less than 25, wherein the second catalyst impregnated on the catalyst support is bis(1-ethylindenyl) zirconium $(CH_3)_2$, bis(1-ethylindenyl) zirconium F_2, bis(1-ethylindenyl) zirconium Cl_2, or any combinations thereof;

wherein the ratio of H_2/C_2 is in ppm/mol%, and wherein the Mw is in g/mol.

2. The polymerization catalyst of claim 1, wherein the catalyst support comprises silica.

3. The polymerization catalyst of claim 1, wherein the catalyst support comprises an aluminoxane.

4. The polymerization catalyst of claim 1, wherein the polyethylene copolymer formed has a molecular weight ratio for a high molecular weight component to a low molecular weight component of between 1:2 and 1:5.

5. The polymerization catalyst of claim 1, wherein the polyethylene copolymer formed has a density of a high molecular weight component that is between 0.02 and 0.05 less than a density of a low molecular weight component.

6. The polymerization catalyst of claim 1, wherein the polyethylene copolymer formed has a high molecular weight component with a weight average molecular weight between 75,000 and 150,000.

7. The polymerization catalyst of claim 1, wherein the polyethylene copolymer formed has a low molecular weight component with a weight average molecular weight between 10,000 and 40,000.

8. The polymerization catalyst of claim 1, wherein the polyethylene copolymer formed has a weight average molecular weight between 90,000 and 110,000.

PRODUCING POLYOLEFIN PRODUCTS

ABSTRACT

Catalyst systems and methods for making and using the same are described. A method includes selecting a catalyst blend using a blend polydispersity index (bPDI) map. The polydispersity map is generated by generating a number of polymers for at least two catalysts. Each polymer is generated at a different hydrogen to ethylene ratio. At least one catalyst generates a higher molecular weight polymer and another catalyst generates a lower molecular weight polymer. A molecular weight for each polymer is measured. The relationship between the molecular weight of the polymers generated by each of the catalysts and the ratio of hydrogen to ethylene is determined. A family of bPDI curves for polymers that would be made using a number of ratios of a blend of the at least two catalysts for each of a number of ratios of hydrogen to ethylene. A ratio for the catalyst blend of the catalysts that generates a polymer having a bPDI that matches a polymer fabrication process is selected, and the product specific polyolefin is made using the catalyst blend.

[Fig. 1]