[0004] For an ethylene alpha-olefin copolymer, short chain branching (SCB) on a polymer chain is typically created through comonomer incorporation during polymerization. Short chain branch distribution (SCBD) refers to the distribution of short chain branches within a molecule or among different molecules that comprise the polyethylene polymer. When the amount of SCB varies among the polyethylene molecules, the resin is said to have a "broad" SCBD. When the amount of SCB is similar among the polyethylene molecules of different chain lengths, the SCBD is said to be "narrow."

[0005] SCBD is known to influence the properties of copolymers, for example, stiffness, toughness, extractable content, environmental stress crack resistance, and heat sealing, among other properties. SCBD 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 MWD and SCBD is largely dictated by the type of catalyst used and is often invariable for a given catalyst system. Ziegler-Natta catalysts and chromium based catalysts produce polymers with broad SCBD, whereas metallocene catalysts normally produce polymers with narrow SCBD. It has been long observed in the industry that there are trade-off paradigms among the different product attributes; most noticeably among stiffness, toughness, and processability (S/T/P). Since the introduction of metallocene in 1990s, some of such paradigms have been relaxed significantly with careful manipulations of molecular structure and composition in the product.

[0007] Polymers having a broad orthogonal composition distribution (BOCD) in which the comonomer is incorporated preferentially in the high molecular weight chains can lead to improved physical properties, for example, stiffness, toughness, processability, and environmental stress crack resistance (ESCR), among others. Because of the improved physical properties of polymers with broad 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 ~~embodiment~~ example described herein provides a polymer that includes ethylene and at least one alpha olefin having from 4 to 20 carbon atoms. The polymer is formed by a trimmed catalyst system including a supported catalyst comprising bis(n-propylcyclopentadienyl)

hafnium (R_1)(R_2) and a trim catalyst comprising meso-O($SiMe_2Ind$)$_2$Zr(R_1)(R_2), wherein R_1 and R_2 are each, independently, methyl, chloro, fluoro, or a hydrocarbyl group.

[0009] Another ~~embodiment~~ example provides a polymer that includes ethylene and at least one alpha olefin having from 4 to 20 carbon atoms. The polymer has been formed from a co-supported catalyst in a single reactor; and has a density between about 0.915 and about 0.935, an average modulus of greater than about 30,000 psi, a dart impact strength of greater than about 350 g/mil, a melt index ratio (MIR) greater than about 15, and an absence of a negative inflection point in a van Gurp Palmen (vGP) plot at a frequency of between about 0.1 rad/s and 200 rad/s at 190 ºC.

[0010] Another ~~embodiment~~ example provides a polymer that includes ethylene and at least one alpha olefin having from 4 to 20 carbon atoms. The polymer has a peak in a first derivative of a van Gurp Palmen (vGP) plot at a frequency of between about 0.1 rad/s and 300 rad/s at 190 ºC. The polymer also has a melt index ratio (MIR) greater than about 15, and a dart impact strength of greater than about 350 g/mil.

[0010a] In one aspect, the present disclosure refers to a polymer, comprising ethylene and at least one alpha olefin having from 4 to 20 carbon atoms, wherein the polymer has: an absence of long chain branching in the polymer as indicated by an absence of an inflection point in a van Gurp Palmen (vGP) plot at a frequency of between 0.1 rad/s and 300 rad/s at 190 ºC and a negative deflection in a first derivative of the vGP plot; a melt index ratio (MIR) from 15 to 80; and a dart impact strength, 26 inch, measured according to ASTM D1709-91, of greater than 350 g/mil.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] 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.

[0012] Fig. 2 is a plot comparing stiffness, toughness, and processability for a number of different polymers.

[0013] Fig. 3 is a van Gurp-Palmen (vGP) plot showing a comparison of products generated in the first pilot plant run.

[0014] Fig. 4 is a plot of the first derivative of the results shown in the vGP plot of Fig. 3.

[0015] Fig. 5 is a plot of the first derivative of the vGP plot for resins made in the second pilot plant run.

[0016] Figs. 6A and 6B are plots that illustrate the calculations used to determine the CFC result.

[0017] Fig. 7 is a plot of (Mw-1/Mw-2) vs. (Tw-1 – Tw-2) for the experimental polymers versus a variety of competitive polymers on the market.

DETAILED DESCRIPTION

[0018] It has been discovered that when a support is impregnated with multiple catalysts, new polymeric materials with improved balance of stiffness, toughness and processability can be achieved, *e.g.*, by controlling the amounts and types of catalysts present on the support. As described in embodiments herein, appropriate selection of the catalysts and ratios may be used to

CLAIMS

What is claimed is:

1. A polymer, comprising ethylene and at least one alpha olefin having from 4 to 20 carbon atoms, wherein the polymer has:

an absence of long chain branching in the polymer as indicated by an absence of an inflection point ~~a peak~~ in a ~~first derivative of a~~ van Gurp Palmen (vGP) plot at a frequency of between ~~about~~ 0.1 rad/s and 300 rad/s at 190 ºC and a negative deflection in a first derivative of the vGP plot;

a melt index ratio (MIR) ~~greater than about 15~~ from 15 to 80; and

a dart impact strength, 26 inch, measured according to ASTM D1709-91, of greater than ~~about~~ 350 g/mil.

2. The polymer of claim 1, wherein the polymer has a relationship between average modulus (M), which is the sum of the 1% secant Modulus measured according to ASTM D-882-91, in the machine direction and in the transverse direction divided by two, and dart impact strength in g/mil (DIS) complying with the formula:

$$DIS \geq 0.8x[100 + e^{(11.71-0.000268xM+2.183x10^{-9}xM^2)}].$$

3. The polymer of claim 1, wherein the polymer has:

a value for Mw1/Mw2 of at least ~~about~~ 1.7, wherein Mw1/Mw2 is a ratio of a weight average molecular weight (Mw) for a first half of a temperature rising elution (TREF) curve to a Mw for a second half of the TREF curve; and

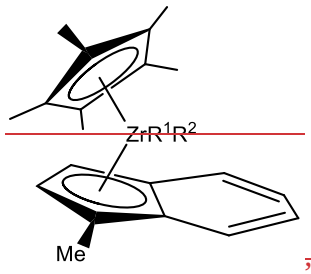
a value for Tw1 – Tw2 of less than ~~about~~ -15 ºC, wherein Tw1 – Tw2 is a difference of a weight average elution temperature (Tw) for the first half of the TREF curve to a Tw for the second half of the TREF curve.

4. The polymer of claim 1, wherein the polymer has:

an average modulus, which is the sum of the 1% secant Modulus measured according to ASTM D-882-91, in the machine direction and in the transverse direction divided by two, of greater than ~~about~~ 20,000 psi; and

a dart drop strength of greater than ~~about~~ 100 g/mil.

~~5. The polymer of claim 1, comprising a polymer chain formed by a catalyst system comprising any one of the compounds represented by the following formulas:~~



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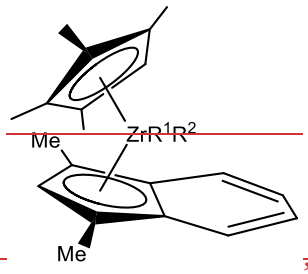

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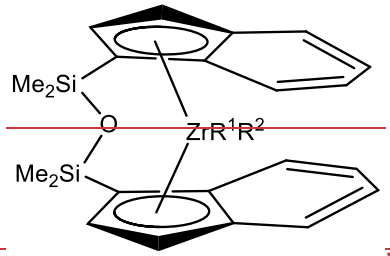

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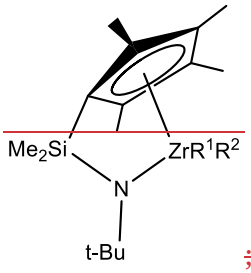

~~; wherein R^1 and R^2 are each, independently, methyl, chloro, fluoro, or a hydrocarbyl group.~~

~~6. The polymer of claim 1, comprising a polymer chain formed by a catalyst system comprising bis(n-propylcyclopentadienyl) hafnium $(CH_3)_2$.~~

~~7. The polymer of claim 1, comprising polymer chains formed by a catalyst system comprising bis(n-propylcyclopentadienyl) hafnium $(CH_3)_2$ and meso-$O(SiMe_2Ind)_2ZrMe_2$.~~