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(57) **Abrégé/Abstract:**

A dual reactor solution process gives high density polyethylene compositions containing a first ethylene polymer and a second ethylene polymer which have a good balance of processability, toughness, and environmental stress crack resistance combined with good organoleptic properties. The polyethylene compositions are suitable for compression molding or injection molding applications and are particularly useful in the manufacture of caps and closures for bottles.



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CLOSURES FOR BOTTLES**ABSTRACT OF THE DISCLOSURE**

A dual reactor solution process gives high density polyethylene compositions containing a first ethylene polymer and a second ethylene polymer which have a good balance of processability, toughness, and environmental stress crack resistance combined with good organoleptic properties. The polyethylene compositions are suitable for compression molding or injection molding applications and are particularly useful in the manufacture of caps and closures for bottles.

FIELD OF THE INVENTION

The present invention relates to polyethylene compositions that are useful in the manufacture of closures for bottles.

BACKGROUND OF THE INVENTION

5 Polymer compositions useful for molding applications, specifically the manufacture of caps and closures for bottles are well known. Screw closures for example, are typically made from polypropylene (PP) in order to achieve the necessary cap strength, however, an inner liner composed of a soft polymer is required to provide necessary seal properties. The
10 soft inner liner can be made from ethylene/vinyl acetate (EVA), polyvinyl chloride (PVC), butyl rubber or other suitable material. The two-part cap is costly, and single part constructions are preferred to reduce cost.

Accordingly, one-piece closures, such as screw caps have more recently been made from polyethylene resins. The use of high density
15 resin is required if the closures are to have sufficient stiffness, while broader molecular weight distributions are desirable to impart good flow properties and to improve environmental stress crack resistance (ESCR).

Polyethylene blends produced with conventional Ziegler-Natta or Phillips type catalysts systems can be made having suitably high density
20 and ESCR properties, see for example, WO 00/71615 and US 5,981,664. However, the use of conventional catalyst systems typically produces significant amounts of low molecular weight polymer chains having high comonomer contents, which results in resins having non-ideal organoleptic properties.

Examples of high density multimodal polyethylene blends made using conventional catalyst systems for the manufacture of caps or closures are taught in US 2005/0004315A1; US 2005/0267249A1; WO 2006/048253, WO 2006/048254 and WO 2007/060007.

5 In contrast to traditional catalysts, the use of so called single site catalysts (such as "metallocene" and "constrained geometry" catalysts) provides resin having lower catalyst residues and improved organoleptic properties as taught by US Pat. No. 6,806,338 and US Pat. No. 7,022,770. The disclosed resins are suitable for use in molded articles.

10 Despite the progress made in the field, there remains a need for new polyethylene resins having an improved balance of toughness, ESCR, processability, and organoleptic properties for use in the manufacture of caps and closures. We have now found that use of a single site catalyst system in a dual reactor solution process, provides bimodal polyethylene
15 compositions of specific molecular weight distributions having good and balanced rheological and mechanical properties. The polyethylene compositions provided also have good organoleptic properties and are especially well suited to the manufacture of closures for bottles.

SUMMARY OF THE INVENTION

20 The present invention provides an improved polyethylene composition that can be used in caps and closures.

The present invention provides caps and closures comprising a polyethylene composition made by a two reactor solution phase process and a single site catalyst. Plaques made from the polyethylene
25 compositions have an improved balance of rheological, processing and

organoleptic properties relative to those made using transitional catalysts and processes.

The current invention provides a closure for bottles, containers and the like, comprising a bimodal polyethylene composition, said bimodal polyethylene composition comprising: (1) 10 to 70 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density of from 0.932 to 0.955 g/cm³; (2) 90 to 30 wt% of a second ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm³; wherein the density of said second ethylene polymer is less than 0.035 g/cm³ higher than the density of said first ethylene polymer; and wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm³; a melt index of from 0.4 to 3 g/10min; and a comonomer content of less than 0.5 mol%.

Provided is a closure for bottles, containers and the like comprising a bimodal polyethylene composition, said polyethylene composition comprising: (1) 20 to 60 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density of from 0.932 to 0.955 g/cm³; (2) 80 to 40 wt% of a second ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm³; wherein the density of said

second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm^3 ; a melt index of from 0.4 to 3 g/10min; and a comonomer content of less than 0.5 mol%; wherein said polyethylene composition is prepared by contacting ethylene and 1-octene under solution polymerization conditions in at least two polymerization reactors.

Provided is a polyethylene composition comprising: (1) 20-60 wt% of a first ethylene polymer having a M_w of at least 110000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density of from 0.932 to 0.955 g/cm^3 ; (2) 80-40 wt% of a second ethylene polymer having a M_w of at most 45000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3 ; wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; wherein said composition has a hexane extractables level of less than 0.55 wt%; a shear viscosity at 10^4 s^{-1} (230°C) of less than 50 (Pa.s) and satisfies the equations: a) the ratio of I_2 of the second ethylene polymer / I_2 of the first ethylene polymer $> 50/1$; and b) the ratio of I_2 of the second ethylene polymer / I_2 of the composition is from 6 to 2500.

A process is provided to prepare a bimodal polyethylene composition, wherein the composition comprises: (1) 20 to 60 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI > 50 and a density of from 0.932 to 0.955 g/cm^3 ; (2) 80 to 40 wt% of a second

ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm³; wherein the density of said second ethylene polymer is less than 0.035 g/cm³ higher than the density of said first ethylene polymer and wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm³; a melt index of from 0.4 to 3 g/10min; and a comonomer content of less than 0.5 mol%; said process comprising contacting at least one single site polymerization catalyst system with ethylene and at least one comonomer under solution polymerization conditions in at least two polymerization reactors.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the relationship between the comonomer content (mol%) and density for polyethylene compositions of the current invention.

Figure 2 shows the relationship between the shear thinning index $SHI_{(1,100)}$ and the melt index, I_2 of polyethylene compositions of the current invention.

DETAILED DESCRIPTION

The present invention is related to caps and closures for bottles and to the polyethylene compositions used to manufacture them. The polyethylene compositions are composed of at least two ethylene copolymer components: a first ethylene polymer and a second ethylene polymer. The polyethylene compositions of the invention have a good balance of processability, toughness, stiffness, environmental stress crack

resistance, and organoleptic properties making them ideal materials for use in manufacturing caps and closures for bottles.

The terms “cap” and “closure” are used interchangeably in the current invention, and both connote any suitably shaped molded article for enclosing, sealing, closing or covering etc., a suitably shaped opening, a
5 suitably molded aperture, an open necked structure or the like used in combination with a container, a bottle, a jar and the like.

The term “homogeneous” or “homogeneously branched polymer” as used herein is defined in US Patent 3,645,992. Accordingly,
10 homogeneously branched polyethylene is a polymer that has a narrow composition distribution. That is, the comonomer is randomly distributed within a given polymer chain and substantially all of the polymer chains have same ethylene/comonomer ratio. The composition distribution of a polymer can be characterized by the short chain distribution index (SCDI)
15 or composition distribution breadth index (CDBI). The CDBI is defined as the weight per cent of the polymer molecules having a comonomer content within 50 per cent of the median total molar comonomer content. The CDBI is determined using techniques well known in the art, particularly temperature rising elution fractionation (TREF) as described in Wild et al.
20 *Journal of Polymer Science, Pol. Phys. Ed. Vol 20, p 441 (1982)* or in US Patent 4,798,081.

The First Ethylene Polymer

In an aspect of the invention, the first ethylene polymer of the polyethylene composition of the current invention is a homogeneous
25 ethylene copolymer having a density of from about 0.932 g/cm³ to about

0.955 g/cm³; a melt index, I_2 , of less than about 0.4 g/10 min; a molecular weight distribution, M_w/M_n , of below about 3.0 and a weight average molecular weight, M_w , that is greater than the M_w of the second ethylene polymer. Preferably, the weight average molecular weight of the first
5 ethylene polymer is at least 110000.

The density of the first ethylene polymer may be measured according to ASTM D792. The melt index, I_2 , of the first ethylene polymer fraction may be measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight).

10 The density and the melt index, I_2 , of the first ethylene polymer can optionally be estimated from GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition (see experimental section).

In another aspect of the invention, the first ethylene polymer of the
15 polyethylene composition is a homogeneous ethylene copolymer having a weight average molecular weight, M_w , of at least 110000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density of from 0.932 to 0.955 g/cm³.

In the present invention, the first ethylene polymer is
20 homogeneously branched ethylene copolymer and can have a CDBI of greater than about 30%, more preferably of greater than about 50%.

The first ethylene polymer can comprise between 10 and 70 weight percent (wt%) of the polyethylene composition, based on the total weight of the first and second ethylene polymers.

The comonomer content in the first ethylene polymer can be from about 0.01 to about 0.25 mol% as measured by NMR, or FTIR or GPC-FTIR methods. The comonomer content of the first ethylene polymer can also be determined by mathematical deconvolution methods applied to a
5 bimodal polyethylene composition (see experimental section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

The Second Ethylene Polymer

In an aspect of the invention, the second ethylene polymer of the
10 polyethylene composition of the current invention is a homogeneous ethylene copolymer having a density below 0.962 g/cm^3 but which is higher than the density of the first ethylene polymer; a melt index, I_2 , of from about 20 to 1000 g/10min.; a molecular weight distribution, M_w/M_n , of below about 3.0 and a number average molecular weight that is less than
15 the M_w of the first ethylene. Preferably, the weight average molecular weight, M_w , will be below 45,000.

The density of the second ethylene polymer may be measured according to ASTM D792. The melt index, I_2 , of the second ethylene polymer may be measured according to ASTM D1238 (when conducted at
20 190°C , using a 2.16 kg weight).

The density and the melt index, I_2 , of the second ethylene polymer can optionally be estimated from GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition.

In another aspect of the invention, the second ethylene polymer of
25 the polyethylene composition is a homogeneous ethylene copolymer

having a weight average molecular weight, M_w , of at most 45000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3 .

In the present invention, the second ethylene polymer is
5 homogeneously branched ethylene copolymer and can have a CDBI of greater than about 30%, more preferably of greater than about 50%.

The second ethylene polymer can comprise between 90 and 30 wt% of the polyethylene composition, based on the total weight of the first and second ethylene polymers.

10 The comonomer content in the second ethylene polymer can be from about 0.01 to about 3 mol% as measured by NMR, or FTIR or GPC-FTIR methods. The comonomer content of the second ethylene polymer can also be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition. The comonomer is one or more
15 suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with the use of 1-octene being preferred.

In an aspect of the invention the second ethylene polymer has a density that is within about 0.035 g/cm^3 higher than the density of the first ethylene polymer.

20 In an aspect of the invention, the I_2 of the second ethylene polymer is at least 10 times, preferably more than 25 times, the I_2 of the first ethylene polymer.

The Polyethylene Composition

The polyethylene composition of this invention has a broad, bimodal
25 or multimodal molecular weight distribution. Minimally, the polyethylene

composition will contain a first ethylene polymer and a second ethylene polymer.

In a specific aspect of the invention, the polyethylene composition is bimodal. In the current invention, the term "bimodal" means that the polyethylene composition comprises at least two components, one of which has a lower molecular weight and a higher density and another of which has a higher molecular weight and a lower density. Typically, a bimodal or multimodal polyethylene composition can be identified by using gel permeation chromatography (GPC). Generally, the GPC chromatograph will exhibit two or more component ethylene polymers, where the number of component ethylene polymers corresponds to the number of discernible peaks. One or more component ethylene polymers may also exist as a hump, shoulder or tail relative to the molecular weight distribution of the other ethylene polymer component.

The polyethylene composition of the current invention has at least the following characteristics: a density of greater than or equal to 0.949 g/cm^3 , as measured according to ASTM D792; a melt index, I_2 , of from about 0.4 to about 5 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C , using a 2.16 kg weight); a molecular weight distribution, M_w/M_n , of from about 3 to about 9 and a comonomer content of less than 0.55 mol% as measured by FTIR or ^{13}C NMR methods, where the comonomer is one or more suitable alpha olefins such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred. Alternatively, the polyethylene composition of the current invention has at least the following characteristics: a hexane

extractables level of less than 0.55 wt%; a shear viscosity at 10^4 s^{-1} (230°C) of less than 50 (Pa.s) and satisfies the equations: a) the ratio of I_2 of the second ethylene polymer / I_2 of the first ethylene polymer $> 50/1$; and b) the ratio of I_2 of the second ethylene polymer / I_2 of the polyethylene composition is from 6 to 2500.

In an aspect of the invention, the polyethylene composition has a melt index, I_5 , of greater than about 1.1 g/10min, as measured according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight).

In an aspect of the invention, the polyethylene composition has a number average molecular weight, M_n , of below about 30,000.

In an aspect of the invention, the polyethylene composition has a melt flow ratio (MFR_2) defined as I_{21} / I_2 of from 20 to 70.

In an aspect of the invention, the polyethylene composition has a melt flow (MFR_5) defined as I_{21} / I_5 of less than 20.

In an aspect of the invention the polyethylene composition has a shear viscosity at 10^4 s^{-1} (230°C) of less than about 60 (Pa.s); and hexane extractables of below 0.55 wt%.

In an aspect of the invention, the polyethylene composition has a melt index, I_2 , of between 0.4 and 3 g/10 min. In another aspect of the invention, the polyethylene composition has a melt index, I_2 , of less than 2 g/10min.

In an aspect of the invention, the polyethylene composition has a MWD of between 4 and 7.

In an aspect of the invention, the polyethylene composition has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.5 mol % as determined by ^{13}C NMR.

In an aspect of the invention, the shear viscosity ratio, $\text{SVR}_{(10, 1000)}$ at 230°C of the polyethylene composition can be from about 5 to 25, preferably, 6 to 20. The shear viscosity ratio $\text{SVR}_{(10, 1000)}$ is determined by taking the ratio of shear viscosity at shear rate of 10s^{-1} and shear viscosity at shear rate of 1000 s^{-1} as measured with a capillary rheometer at constant temperature (e.g. 230°C), and a die with L/D ratio of 20 and diameter of 0.06".

In an aspect of the invention, the shear thinning index, $\text{SHI}_{(1, 100)}$ of the polyethylene composition is less than about 10; in another aspect the $\text{SHI}_{(1, 100)}$ will be less than about 7. The shear thinning index (SHI), was calculated using dynamic mechanical analysis (DMA) frequency sweep methods as disclosed in PCT applications WO 2006/048253 and WO 2006/048254.

The SHI value is obtained by calculating the complex viscosities $\eta(1)$ and $\eta(100)$ at a constant shear stress of 1 kPa and 100 kPa, respectively.

In an aspect of the invention, the $\text{SHI}_{(1, 100)}$ of the polyethylene composition satisfies the equation: $\text{SHI}_{(1, 100)} < -10.58 \log(I_2 \text{ of polyethylene composition}) + 12.94$. In another aspect of the invention, the $\text{SHI}_{(1, 100)}$ of the polyethylene composition satisfies the equation: $\text{SHI}_{(1, 100)} < -5.5 \log(I_2 \text{ of polyethylene composition}) + 9.66$.

In an aspect of the invention, the I_2 of the second ethylene polymer will be less than 200 times the I_5 of the polyethylene composition.

In an aspect of the invention, a molded article made from the polyethylene composition, has an environment stress crack resistance (ESCR) A10 of at least 20 hrs as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition A).

In an aspect of the invention, a molded article made from the polyethylene composition has an Izod impact strength of at least 50 J/m, as measured according to ASTM D256; a melt index, I_2 , of from 1 to 3 g/10 min and a molecular weight distribution of from 5 to 8.

In another aspect of the invention, a molded article made from the polyethylene composition has a notched Izod impact strength of at least 100 J/m, as measured according to ASTM D256; a melt index, I_2 , of from 0.4 to 1 g/10 min; and a molecular weight distribution of from 3 to 6.

In an aspect of the invention the polyethylene composition of the current invention has a density of between 0.950 and 0.953 g/cm³; a melt index, I_2 , of from 0.4 to 1 g/10 min; a molecular weight distribution of from 3 to 6; a number average molecular weight, M_n , of below 30,000; a shear viscosity at 10⁴s⁻¹ (230°C) of less than 50 (Pa.s) and hexane extractables of less than 0.55 % and a molded article made there from has a notched Izod impact strength of more than 100 J/m and an A10 ESCR of at least 20hrs.

In another aspect of the invention the polyethylene composition of the current invention has a density of between 0.950 and 0.953 g/cm³; a melt index, I_2 , of from 1 to 3 g/10 min; a molecular weight distribution of

from 5 to 8; a number average molecular weight, M_n , of below 30,000; a shear viscosity at 10^4 s^{-1} (230°C) of less than 45 (Pa.s) and hexane extractables of less than 0.55 % and a molded article made there from has an Izod impact strength of more than 60 J/m and an ESCR of at least 20
5 hrs.

The polyethylene composition of this invention can be made using any conventional blending method such as but not limited to physical blending and in-situ blending by polymerization in multi reactor systems. For example, it is possible to perform the mixing of the first ethylene
10 polymer with the second ethylene polymer by molten mixing of the two preformed polymers. Preferred are processes in which the first and second ethylene polymers are prepared in at least two sequential polymerization stages, however, both in-series or an in-parallel dual reactor process are contemplated for use in the current invention. Gas
15 phase, slurry phase or solution phase reactor systems may be used, with solution phase reactor systems being preferred.

In an aspect of the current invention, a dual reactor solution process is used as has been described in for example US Patent No. 6,372,864 and US app. No. 20060247373A1.

20 The homogeneously branched ethylene polymers can be prepared using any catalyst capable of producing homogeneous branching. Generally, the catalysts will be based on a group 4 metal having at least one cyclopentadienyl ligand that is well known in the art. Examples of such catalysts which include metallocenes, constrained geometry catalysts

and phosphinimide catalysts are typically used in combination with methylaluminoxanes, boranes or ionic borate salts and are further described in US Patents 3,645,992; 5,324,800; 5,064,802; 5,055,438; 6,689,847; 6,114,481 and 6,063,879. Such catalysts may also be referred to as “single site catalysts” to distinguish them from traditional Ziegler-Natta or Phillips catalysts which are also well known in the art. In general single site catalysts produce ethylene copolymers having a molecular weight distribution (M_w/M_n) of less than about 2.5 and a composition distribution breadth index (CDBI) of greater than about 30%, preferably greater than 50%.

In an aspect of the current invention, homogeneously branched ethylene polymers are prepared using an organometallic complex of a group 3, 4 or 5 metal that is further characterized as having a phosphinimide ligand.

In an aspect of the invention, use of a single site catalyst that does not produce long chain branching (LCB) is preferred. Without wishing to be bound by any single theory, long chain branching can increase viscosity at low shear rates, thereby negatively impacting cycle times during the manufacture of caps and closures, such during the process of compression molding. Long chain branching is determined using ^{13}C NMR methods and can be quantitatively assessed using the method disclosed by Randall in Rev. Macromol. Chem. Phys. C29 (2 and 3), p. 285.

In an aspect of the invention, the polyethylene composition will contain fewer than 0.3 long chain branches per 100 carbon atoms. In

another aspect of the invention, the polyethylene composition will contain fewer than 0.01 long chain branches per 1000 carbon atoms.

In an aspect of this invention a group IV phosphinimide catalyst system is used in a solution phase dual reactor system to prepare a
5 bimodal polyethylene composition by polymerization of ethylene in the presence of 1-octene.

The production of the polyethylene composition of the present invention will typically include an extrusion or compounding step. Such steps are well known in the art.

10 The polyethylene composition can comprise further polymer components in addition to the first and second ethylene polymers. Such polymer components include polymers made in situ or polymers added to the polymer composition during an extrusion or compounding step.

Optionally, additives can be added to the polyethylene composition.
15 Additives can be added to the polyethylene composition during an extrusion or compounding step, but other suitable known methods will be apparent to a person skilled in the art. The additives can be added as is or as part of a separate polymer component (i.e. not the first or second ethylene polymers described above) added during an extrusion or
20 compounding step. Suitable additives are known in the art and include but are not-limited to antioxidants, phosphites and phosphonites, nitrones, antacids, UV light stabilizers, UV absorbers, metal deactivators, dyes, fillers and reinforcing agents, nano-scale organic or inorganic materials, antistatic agents, lubricating agents such as calcium stearates, slip
25 additives such as erucimide, and nucleating agents. The additives that

can be optionally added are typically added in amount of up to 20 weight percent (wt%).

In an aspect of the invention, the polymer compositions described above are used in the formation of molded articles. For example, articles
5 formed by compression molding and injection molding are contemplated. Such articles include, for example, caps (i.e. screw caps) and closures for bottles. However, a person skilled in the art will readily appreciate that the compositions described above may also be used for other applications such as but not limited to film, blow molding and sheet extrusion
10 applications.

The closures of the current invention can be made according to any known method, including for example injection molding and compression molding techniques that are well known to persons skilled in the art.

The closures of the invention comprise the polyethylene
15 composition described above and have good organoleptic properties, good toughness, as well as good ESCR values. Hence the closures and caps of the current invention are well suited for sealing bottles containing drinkable water, soft drinks and other foodstuffs, including but not limited to liquids that are under pressure (i.e. carbonated beverages).

20 The invention is further illustrated by the following non-limiting examples.

EXAMPLES

M_n , M_w , and M_z (g/mol) were determined by high temperature Gel Permeation Chromatography with differential refractive index detection
25 using universal calibration (e.g. ASTM –D6474-99). The molecular weight

distribution (MWD) is the weight average molecular weight divided by the number average molecular weight, M_w/M_n .

Primary melting peak ($^{\circ}\text{C}$), heat of fusion (J/g) and crystallinity (%) was determined using differential scanning calorimetry (DSC) as follows:

5 the instrument was first calibrated with indium; after the calibration, a polymer specimen is equilibrated at 0°C and then the temperature was increased to 200°C at a heating rate of 10°C/min ; the melt was then kept isothermally at 200°C for five minutes; the melt was then cooled to 0°C at a cooling rate of 10°C/min and kept at 0°C for five minutes; the specimen
10 was then heated to 200°C at a heating rate of 10°C/min . The DSC T_m , heat of fusion and crystallinity are reported from the 2nd heating cycle.

The short chain branch frequency (SCB per 1000 carbon atoms) of copolymer samples was determined by Fourier Transform Infrared Spectroscopy (FTIR) as per the ASTM D6645-01 method. A Thermo-
15 Nicolet 750 Magna-IR Spectrophotometer equipped with OMNIC version 7.2a software was used for the measurements.

Comonomer content can also be measured using ^{13}C NMR techniques as discussed in Randall, Rev. Macromol. Chem. Phys., C29 (2&3), p 285; U.S. Pat. No. 5,292,845 and WO 2005/121239.

20 Polyethylene composition density (g/cm^3) was measured according to ASTM D792.

Hexane extractables were determined according to ASTM D5227.

Shear viscosity was measured by using a Kayeness WinKARS Capillary Rheometer (model # D5052M-115). The die has a die diameter
25 of 0.06 inch and L/D ratio of 20 and an entrance angle of 180 degrees.

Melt indexes, I_2 , I_6 and I_{21} for the polyethylene composition were measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg, a 6.48 kg and a 21 kg weight respectively). The melt index, I_5 , was calculated using the equation: $(5 / 6.48) \times I_6$ or $0.7716 \times I_6$. The melt
 5 index, I_2 and density of the first and second ethylene polymers were estimated by GPC-FTIR deconvolution experiments as discussed below.

High temperature GPC equipped with an online FTIR detector (GPC-FTIR) was used to measure the comonomer content as the function of molecular weight. Mathematical deconvolutions are performed to
 10 determine the relative amount of polymer, molecular weight and comonomer content of the component made in each reactor, by assuming that each polymer component follows a Flory's molecular weight distribution function and it has a homogeneous comonomer distribution across the whole molecular weight range.

15 For these SSC catalyzed resins, the GPC data from GPC-FTIR chromatographs was fit based on Flory's molecular weight distribution function.

To improve the deconvolution accuracy and consistency, as a constraint, the melt index, I_2 , of the targeted resin was set and the
 20 following relationship was satisfied during the deconvolution:

$$\begin{aligned} \text{Log}_{10}(I_2) = & 22.326528 + 0.003467 \cdot [\text{Log}_{10}(M_n)]^3 - 4.322582 \cdot \text{Log}_{10}(M_w) - \\ & 0.180061 \cdot [\text{Log}_{10}(M_z)]^2 + 0.026478 \cdot [\text{Log}_{10}(M_z)]^3 \end{aligned}$$

where the experimentally measured overall melt index, I_2 , was used on the left side of the equation, while M_n of each component ($M_w = 2 \times M_n$ and $M_z =$
 25 $1.5 \times M_w$ for each component) was adjusted to change the calculated

overall M_n , M_w and M_z of the composition until the fitting criteria were met. During the deconvolution, the overall M_n , M_w and M_z are calculated with the following relationships: $M_n = 1/\text{Sum}(w_i/M_n(i))$, $M_w = \text{Sum}(w_i \times M_w(i))$, $M_z = \text{Sum}(w_i \times M_z(i)^2)$, where i represents the i -th component and w_i represents

5 the relative weight fraction of the i -th component in the composition.

The uniform comonomer distribution (which results from the use of a single site catalyst) of the resin components allowed the estimation of the short chain branching content (SCB), in branches per 1000 carbon atoms and calculation of comonomer content (in mol%) and density (in

10 g/cm^3) for the first and second ethylene polymers, based on the deconvoluted relative amounts of first and second ethylene polymer components in the polyethylene composition, and their estimated resin molecular weight parameters from the above procedure.

A component (or composition) density model and a component (or

15 composition) melt index, I_2 , model was used according to the following equations to calculate the density and melt index of the first and second ethylene polymers:

$$\begin{aligned} \text{density} = & 0.979863 - 0.00594808 \cdot (\text{FTIR SCB}/1000\text{C})^{0.65} - \\ & 0.000383133 \cdot [\text{Log}_{10}(M_n)]^3 \\ & - 0.00000577986 \cdot (M_w/M_n)^3 + 0.00557395 \cdot (M_z/M_w)^{0.25} \\ \text{Log}_{10}(\text{melt index, } I_2) = & 22.326528 + 0.003467 \cdot [\text{Log}_{10}(M_n)]^3 - \\ & 4.322582 \cdot \text{Log}_{10}(M_w) - 0.180061 \cdot [\text{Log}_{10}(M_z)]^2 + 0.026478 \cdot [\text{Log}_{10}(M_z)]^3 \end{aligned}$$

20

where the M_n , M_w and M_z were the deconvoluted values of the individual ethylene polymer components, as obtained from the results of the above

25 GPC deconvolution. Hence, these two models were used to estimate the

melt indexes (except for that of the overall composition, where the model is used as a constraint) and the densities of the components and the composition.

Plaques molded from the polyethylene compositions were tested according to the following ASTM methods: Bent Strip Environmental Stress Crack Resistance (ESCR), ASTM D1693; notched Izod impact properties, ASTM D256; Flexural Properties, ASTM D 790; Tensile properties, ASTM D 638; Vicat softening point, ASTM D 1525; Heat deflection temperature, ASTM D 648; Shore D hardness, ASTM D 2240.

Examples of the bimodal polyethylene compositions were produced in a dual reactor solution polymerization process in which the contents of the first reactor flow into the second reactor. This "dual reactor" process produces an "in-situ" polyethylene blend (i.e. the polyethylene composition). Each reactor is sufficiently agitated to give conditions in which components are well mixed. The volume of the first reactor was 12 liters and the volume of the second reactor was 24 liters. These are the pilot plant scales. The first reactor was operated at a pressure of 10500 to 35000 kPa and the second reactor was operated at a lower pressure to facilitate continuous flow from the first reactor to the second. The solvent employed was methylpentane. The process operates using continuous feed streams. The catalyst employed in the dual reactor solution process experiments was a titanium complex having a phosphinimide ligand, a cyclopentadienide ligand and two activatable ligands, such as but not limited to chloride ligands. A boron based co-catalyst was used in approximately stoichiometric amounts relative to the titanium complex.

Commercially available methylaluminoxane (MAO) was included as a scavenger at an Al:Ti of about 40:1. In addition, 2,6-di-tert-butylhydroxy-4-ethylbenzene was added to scavenge free trimethylaluminum within the MAO in a ratio of Al:OH of about 0.5:1.

5 The polymerization conditions are provided in Table 1. The resulting polyethylene compositions are described in Table 2. Estimated properties for the first ethylene polymer and the second ethylene polymer as obtained from GPC-FTIR deconvolution studies are provided in Table 3. The properties of pressed plaques made from the polyethylene
10 compositions is provided in Table 4. Commercially available resin from INEOS, Eltex™ B4020N1331 is included in Tables 2 and 4 for comparison purposes. Eltex™ B4020N1331 is a uni-modal, ZN butene copolymer used widely in the cap industry.

TABLE 1

Reactor Conditions

Experiment	1	2	3	4
Polyethylene Composition	PS 78292	PS 78278	PS 78483	PS 78302
Reactor 1				
Ethylene (kg/h)	38.1	39.2	39.2	39.7
Octene (kg/h)	4.2	2.1	2.6	1.4
Hydrogen (g/h)	0.54	0.79	0.34	0.44
Solvent (kg/h)	302.3	314.2	313.7	319.7
Reactor Feed Inlet Temperature (°C)	30	30	30	30
Reactor Temperature (°C)	149.3	149.3	148.2	149.7
Titanium Catalyst (ppm)	0.06	0.04	0.04	0.04
Reactor 2				
Ethylene (kg/h)	50.3	47.9	47.6	48.5
Octene (kg/h)	5.5	2.6	3.2	1.7
Hydrogen (g/h)	24.72	12	18	7.26
Solvent (kg/h)	163	109.3	106.5	103.6
Reactor Feed Inlet Temperature (°C)	30	29.7	30.5	30
Reactor Temperature (°C)	200.3	209.9	210	210.4
Titanium Catalyst (ppm)	1.10	1.10	1.10	1.10

TABLE 2
Resin Properties

	Comparative Example 1	Comparative Example 2	Inventive Composition 1	Comparative Example 3	Inventive Composition 2
Polyethylene Composition	unimodal, N1331	PS 78292	PS-78278	PS-78483	PS-78302
Density (g/cm ³)	0.9533	0.952	0.9534	0.953	0.9523
Molecular weight profile	unimodal	bimodal	bimodal	bimodal	bimodal
Melt Index I ₂ (g/10 min)	2.45	1.92	1.88	0.68	0.625
Melt Flow Ratio (I ₂₁ /I ₂)	32.5	77.1	56.9	73.2	51.2
Shear Viscosity at 10 ⁴ s ⁻¹ (230°C, Pa-s)	45.9	26.6	37.3	35.50	43.60
Zero Shear Viscosity, 190°C (Pa-s)	6193	5582	5896.0	14360	17250
Shear Viscosity Ratio, 200°C	7.42	17.56	13.14	24.89	19.0
Shear Viscosity Ratio, 230°C	6.3	14.21	11.58		17.0
Shear Viscosity Ratio, 250°C	6.11	12.62	9.79	20.23	15.56
M _n	23548	9891	14393	12424	22392
M _w	89571	77319	91663	104353	109626
M _z	319120	245479	325841	327007	299470
Polydispersity Index (M _w /M _n)	3.8	7.82	6.37	8.4	4.9
Comonomer content (mol%) by FTIR	< 0.1	0.7	0.4	0.5	0.4
Comonomer type	butene	Octene	octene	octene	octene
Comonomer content (mol%) by ¹³ C NMR; for comonomer with ≥ 4 carbon atoms			0.3		0.2
SCB per 1000 carbon atoms by FTIR	< 0.5	3.7	2.2	2.5	2
Primary Melting Peak (°C)	130.35	126.8	128.3	128.42	129.7
Heat of Fusion (J/g)	206.3	200.3	204.7	213.80	198.2
Crystallinity (%)	71.14	69.08	70.58	73.72	68.34
Hexane Extractables (%)	0.35	0.73	0.44	0.57	0.46
VICAT Soft. Pt. (°C) - Plaque	127	122	126	125	127
Shore D Hardness - Plaque	68.5	67.1	68	67.2	67.9
Cold Brittleness Temp. (-70°C) - Plaque	pass at -70C	pass at -70C	pass at -70C	pass at -70C	pass at -70C
Heat Deflection Temp. [C] @ 66 PSI	72	68	72	71	71

TABLE 3**Polyethylene Component Properties**

Polyethylene Composition	PS 78292 (Comparative)	PS-78278 (Inventive)	PS-78483 (Comparative)	PS-78302 (Inventive)
First Ethylene Polymer				
Wt%	0.43	0.43	0.45	0.43
M_w	169500	162400	213200	214300
melt index, I_2 (g/10min.)	0.11	0.13	0.05	0.05
density 1 (g/cm ³)	0.9382	0.9389	0.9363	0.9356
Short chain branches per 1000 Cs	0.18	0.15	0.06	0.13
Second Ethylene Polymer				
Wt%	0.57	0.57	0.55	0.57
M_w	11700	18500	14300	25600
melt index, I_2 (g/10min.)	5082	736	2148	190
density 2 (g/cm ³)	0.9559	0.9559	0.9565	0.9522
Short chain branches per 1000 Cs	2.1	1.06	1.42	1.37
Estimated (d2 - d1), g/cm ³	0.0177	0.017	0.0202	0.0166
Estimated (SCB2 - SCB1)/1000C	1.92	0.91	1.36	1.24

TABLE 4**Plaque Properties**

Polyethylene Composition	N1331 (Comparative)	PS 78292 (Comparative)	PS-78278 (Inventive)	PS-78483 (Comparative)	PS-78302 (Inventive)
ESCR Cond. A at 10 % (hrs)	<23	<24	<24	64.5	40
ESCR Cond. A at 100 % (hrs)	<23	75 < F50 < 139	<24	324.1	68.4
ESCR Cond. B at 10 % (hrs)	<24	<24	<24	< 24	<24
ESCR Cond. B at 100 % (hrs)	<24	184.1	28.1	318.8	76.3
Flexural Properties (Plaques)					
Flex Secant Mod. 1% (MPa)	1298	1062	1035	1201	1070
Flex Sec Mod 1% (MPa) Dev.	39	34	25	41	37
Flex Secant Mod. 2% (MPa)	1083	904	877	1002	906
Flex Sec Mod 2% (MPa) Dev.	24	28	19	32	29
Tensile Properties (Plaques)					
Yield Strength (MPa)	27.7	25.7	26.6	26.9	25.4
Yield Strength Dev. (MPa)	0.2	0.6	0.3	0.3	0.4
Elong. at Yield (%)	10.1	10.3	10.2	10.2	10.3
Elong. at Yield Dev. (%)	0.6	0.3	0.8	0.4	1
Ultimate Strength (MPa)	33.2	14.8	21.5	800	1003
Ultimate Strength Dev. (MPa)	0.6	0.7	4.1	86.1	23.7
Sec Mod 1% (MPa)	1413	1244	1374	1237	1138
Sec Mod 1% (MPa) Dev.	182.5	47.1	276.4	83	210.8
Sec Mod 2% (MPa)	949	858	937	888	834
Sec Mod 2% (MPa) Dev.	38.9	24	71	47	61
Ultimate Elong. (%)	1407	535	920	800	1003
Ultimate Elong.Dev. (%)	40.7	167.4	94.6	86.1	23.7
Izod Impact (J/m)	76	69	76	97	139
IZOD DV (J/m)	2	7	7	3	7

Comonomer Content

As shown in Figure 1, the polyethylene compositions PS-78278 and PS-78302 do not satisfy equation: comonomer mol% > $-0.0612 d [\text{kg/m}^3] + 58.6$ under conditions in which the comonomer content (for comonomers of at least 4 carbon atoms) is more than 0.5 mol%, which is a property of the blends taught in WO 2006/048250. The comonomer content in Figure 1 was determined by C^{13} NMR, but if FTIR methods are employed a comonomer content of less than 0.5 mol% is also observed for PS-78278 and PS-78302.

10 Shear Thinning Index

As shown in Figure 2, the polyethylene compositions, PS-78278 and PS-78302 do not satisfy the equation $\text{SHI}_{(1, 100)} \geq -10.58 \log I_2 + 12.94$, which is a property of the blends taught in WO 2006/048253 and WO 2006/048254.

15 Melt Index

The ratio of the melt index, I_2 , of the second ethylene polymer to the calculated melt index, I_5 , of the polyethylene compositions PS-78278 and PS- 78302 is below 200. This is divergent from the teaching of WO/2006/048255, which discloses blends having a ratio of melt index, I_2 , of a low molecular weight component to the melt index, I_5 , of the overall polyethylene composition of more than 200.

The polyethylene compositions, PS-78278 and PS- 78302 have a calculated melt index, I_5 , of above 1.1 g/10min and a ratio of melt index, I_{21} , of the polyethylene composition to the melt index, I_5 , of the polyethylene composition of below 20 (i.e. $I_{21} / I_5 < 20$). This is divergent

from the teaching of WO/2006/048259, which discloses blends having the properties: composition I₅ = 0.5 to 1.1 g/10min; and composition I₂ / composition I₅ = 15 to 28.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A closure comprising a bimodal polyethylene composition, said bimodal polyethylene composition comprising:

- (1) 10 to 70 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density of from 0.932 to 0.955 g/cm³; and
- (2) 90 to 30 wt% of a second ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm³;

wherein the density of said second ethylene polymer is less than 0.035 g/cm³ higher than the density of said first ethylene polymer; and wherein said polyethylene composition has a molecular weight distribution, M_w/M_n , of from 3 to 7; a density of more than 0.949 g/cm³; a melt index, I_2 , of from 0.4 to 3 g/10 min and a comonomer content of less than 0.5 mol%.

2. The closure of claim 1, wherein said polyethylene composition has a molecular weight distribution, M_w/M_n , of from 4 to 7.

3. The closure of claim 1, wherein said polyethylene composition has melt index, I_2 , of from 0.4 to 2 g/10min.

4. The closure of claim 1, wherein the density of said second ethylene polymer is less than 0.030 g/cm^3 higher than the density of said first ethylene polymer.
5. The closure of claim 1, wherein the polyethylene composition has a hexane extractables level of less than 0.55 wt%.
6. The closure of claim 1, wherein the polyethylene composition comprises:
 - from 20 to 60 wt% of a first ethylene polymer; and
 - from 80 to 40 wt% of a second ethylene polymer.
7. The closure of claim 1, wherein the first and second ethylene polymers are copolymers of ethylene and 1-octene.
8. The closure of claim 1, wherein the closure is made by compression molding or injection molding.
9. A closure comprising a bimodal polyethylene composition, said polyethylene composition comprising:
 - (1) 20 to 60 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density of from 0.932 to 0.955 g/cm^3 ; and

(2) 80 to 40 wt% of a second ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10 min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3 ;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm^3 ; a melt index, I_2 , of from 0.4 to 3 g/10min; and a comonomer content of less than 0.5 mol%, and wherein said polyethylene composition is prepared by contacting ethylene and 1-octene under solution polymerization conditions in at least two polymerization reactors.

10. A polyethylene composition comprising:

- (1) 20-60 wt% of a first ethylene polymer having a M_w of at least 110000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density of from 0.932 to 0.955 g/cm^3 ; and
- (2) 80-40 wt% of a second ethylene polymer having a M_w of at most 45000; a molecular weight distribution, M_w/M_n , of less than 2.5 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3 ;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and

wherein said polyethylene composition has a hexane extractables level of less than 0.55 wt%; a shear viscosity at 10^4s^{-1} (230°C) of less than 50 (Pa.s) and satisfies the equations:

- a) the ratio of I_2 of the second ethylene polymer / I_2 of the first ethylene polymer $> 50/1$; and
- b) the ratio of I_2 of the second ethylene polymer / I_2 of the composition is from 6 to 2500.

11. The polyethylene composition of claim 10, wherein said composition has a density of more than 0.949 g/cm^3 .

12. The polyethylene composition of claim 11, wherein said composition has a molecular weight distribution, M_w/M_n , of 3 to 7.

13. The polyethylene composition of claim 12, wherein the composition has a melt index, I_2 , of 0.4 to 3 g/10min.

14. The polyethylene composition of claim 13, wherein the first and second ethylene polymers are copolymers of ethylene and 1-octene.

15. A compression molded or injection molded closure for bottles comprising the polyethylene composition of claims 10-14.

16. A process to prepare a bimodal polyethylene composition, wherein the composition comprises:

- (1) 20 to 60 wt% of a first ethylene polymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density of from 0.932 to 0.955 g/cm³; and
- (2) 80 to 40 wt% of a second ethylene polymer having a melt index, I_2 , of from 20 to 1000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; a CDBI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm³;

wherein the density of said second ethylene polymer is less than 0.035 g/cm³ higher than the density of said first ethylene polymer; and wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm³; a melt index, I_2 , of from 0.4 to 3 g/10min and a comonomer content of less than 0.5 mol%; and said process comprising contacting at least one single site polymerization catalyst system with ethylene and at least one comonomer under solution polymerization conditions in at least two polymerization reactors.

- 17. The process of claim 16, wherein the comonomer is 1-octene.
- 18. A process for preparing the closure of claim 1 or 9, wherein the process comprises at least one compression molding or injection molding step.

FIGURE 1

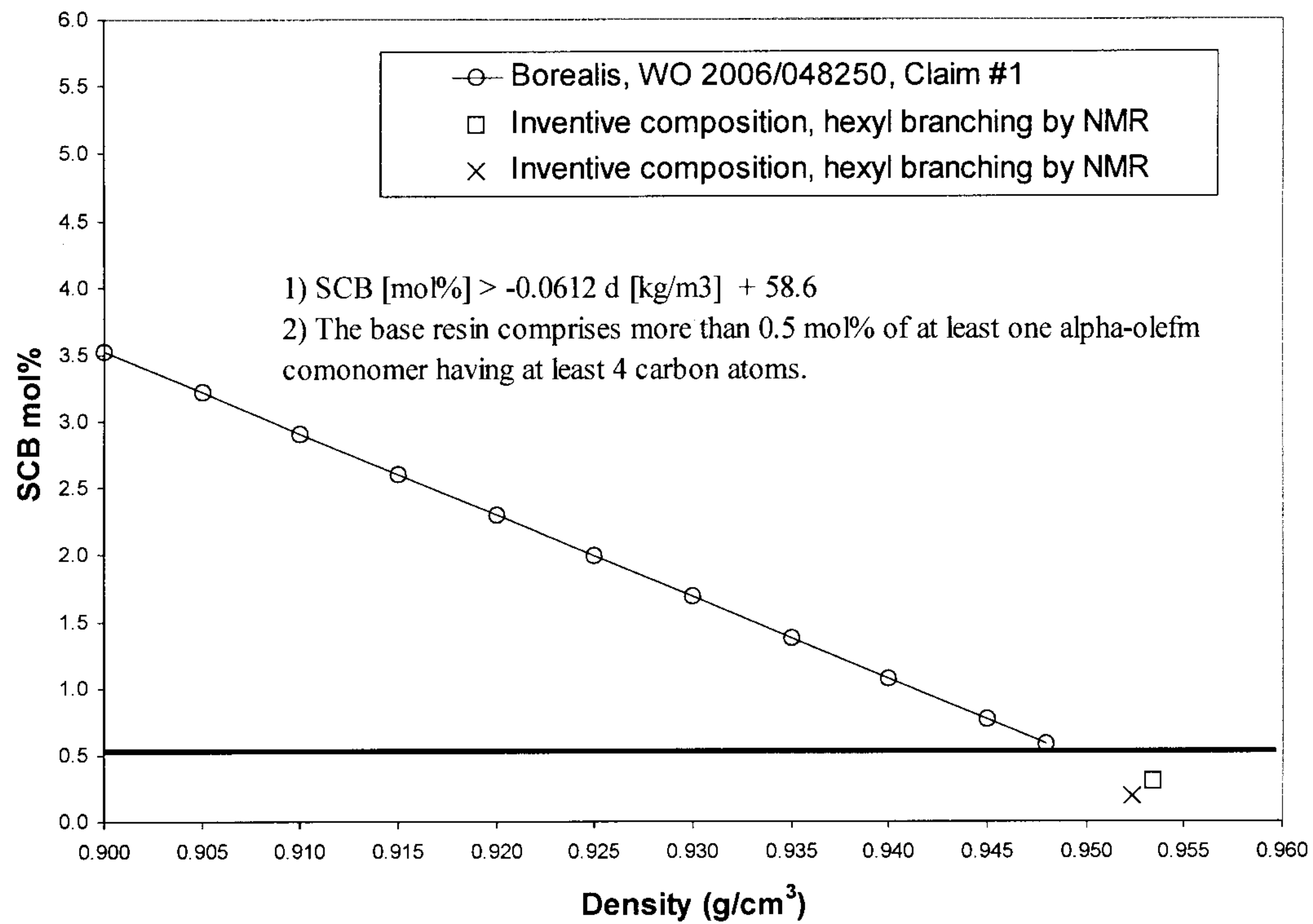


FIGURE 2

