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(72) **Inventeurs/Inventors:**
WANG, XIAOCHUAN, CA;
LACOMBE, YVES, CA;
WEBER, MARK EDMUND, CA

(73) **Propriétaire/Owner:**
NOVA CHEMICALS CORPORATION, CA

(74) **Agent:** BAAR, CLIFF

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(54) **Title:** POLYETHYLENE COMPOSITIONS AND CLOSURES FOR BOTTLES

(57) **Abrégé/Abstract:**

A dual reactor solution process gives high density polyethylene compositions containing a first ethylene copolymer and a second ethylene copolymer and which have good 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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POLYETHYLENE COMPOSITIONS AND CLOSURES FOR BOTTLES

ABSTRACT OF THE DISCLOSURE

20 A dual reactor solution process gives high density polyethylene compositions containing a first ethylene copolymer and a second ethylene copolymer and which have good 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

25 manufacture of caps and closures for bottles.

POLYETHYLENE COMPOSITIONS AND CLOSURES FOR BOTTLES

FIELD OF THE INVENTION

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

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BACKGROUND OF THE INVENTION

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
10 necessary seal properties. The 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 resin is required if the closures
15 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 and ESCR properties, see
20 for example, WO 00/71615 and U.S. Pat. No. 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
25 conventional catalyst systems for the manufacture of caps or closures are taught in U.S. Pat. Nos 2005/0004315A1; 2005/0267249A1; as well as WO 2006/048253, WO

2006/048254, WO 2007/060007; and EP 2,017,302A1. Further high density, multimodal polyethylene blends made by employing conventional Ziegler-Natta catalysts are disclosed in U.S. Pat. Nos. 2009/0062463A1; 2009/0198018; 2009/0203848 and in WO 2007/130515, WO 2008/136849 and WO 2010/088265.

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 U.S. Pat. No. 6,806,338. The disclosed resins are suitable for use in molded articles. Further resins comprising metallocene catalyzed components and which are useful for molding
10 applications are described in U.S. Pat. Nos. 7,022,770; 7,307,126; 7,396,878 and 7,396,881.

U.S. Pat. Appl. No. 2011/0165357A1 discloses a blend of metallocene catalyzed resins which is suitable for use in pressure resistant pipe applications.

U.S. Pat. Appl. No. 2006/0241256A1 teaches blends formulated from
15 polyethylenes made using a hafnocene catalyst in the slurry phase.

A bimodal resin having a relatively narrow molecular weight distribution and long chain branching is described in U.S. Pat. No. 7,868,106. The resin is made using a bis-indenyl type metallocene catalyst in a dual slurry loop polymerization process and can be used to manufacture caps and closures.

20 Narrow molecular weight polyethylene blends comprising a metallocene produced polyethylene component and a Ziegler-Natta or metallocene produced polyethylene component are reported in U.S. Pat. No. 7,250,474. The blends can be used in blow molding and injection molding applications such as for example, milk bottles and bottle caps respectively.

25 In U.S. Pat. Appl. No. 2010/0261848A1 we disclosed a resin composition having a good balance of toughness, ESCR, processability, and organoleptic properties for use

in the manufacture of caps and closures. The resins were made using a single site catalyst system in a dual reactor solution process, to provide bimodal polyethylene compositions in which comonomer was present in both a high and a low molecular weight component. The disclosed resins had a normal comonomer distribution in that

5 the low molecular weight component had a larger amount of comonomer than did the high molecular weight component. We have now found that by adding more comonomer to the high molecular weight component of these resins, we can improve the ESCR properties. The polyethylene compositions provided by the present invention also have good organoleptic properties, balanced rheological and mechanical

10 properties and are suitable for use in the manufacture of closures for bottles.

SUMMARY OF THE INVENTION

The present invention provides a polyethylene composition that can be used in the manufacture of caps and closures for bottles.

The present invention provides a polyethylene composition which has an

15 improved ESCR while maintaining low shear viscosity values at high shear rates which is desirable for high-speed injection or compression molding applications.

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 compositions have a good balance of mechanical,

20 processing and organoleptic properties.

Provided is a closure for bottles, the closure comprising a bimodal polyethylene composition comprising:

(1) 10 to 70 wt% of a first ethylene copolymer 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; and a

25 density of from 0.920 to 0.955 g/cm³; and

- (2) 90 to 30 wt% of a second ethylene copolymer having a melt index I_2 , of from 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; and a density higher than the density of the first ethylene copolymer, but less than 0.967 g/cm³;
- 5 wherein the density of the second ethylene copolymer is less than 0.037 g/cm³ higher than the density of the first ethylene copolymer; the ratio of short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) is greater than 0.5; and wherein the bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 3 to 11; a
- 10 density of at least 0.949 g/cm³; a melt index of from 0.4 to 5.0 g/10 min; an M_z of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAI) of at least 20 hrs.

Provided is a process to prepare a polyethylene composition, the polyethylene composition comprising:

- 15 (1) 10 to 70 wt% of a first ethylene copolymer 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; and a density of from 0.920 to 0.955 g/cm³; and
- (2) 90 to 30 wt% of a second ethylene copolymer having a melt index I_2 , of
- 20 from 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; and a density higher than the density of the first ethylene copolymer, but less than 0.967 g/cm³; wherein the density of the second ethylene copolymer is less than 0.037 g/cm³ higher than the density of the first ethylene copolymer; the
- ratio of short chain branching in the first ethylene copolymer (SCB1) to the short
- 25 chain branching in the second ethylene copolymer (SCB2) is greater than 0.5; and wherein the bimodal polyethylene composition has a molecular weight

distribution, M_w/M_n , of from 3 to 11; a density of at least 0.949 g/cm^3 ; a melt index of from 0.4 to 5.0 g/10 min; an Mz of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAL) of at least 20 hrs;

the process comprising contacting at least one single site

5 polymerization catalyst system with ethylene and at least one
alpha-olefin comonomer under solution polymerization conditions
in at least two polymerization reactors.

Provided is a bimodal polyethylene composition comprising:

(1) 30 to 60 wt% of a first ethylene copolymer having a melt index, I_2 , of less
10 than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 2.7; and a
density of from 0.925 to 0.950 g/cm^3 ; and

(2) 70 to 40 wt% of a second ethylene copolymer having a melt index I_2 , of
from 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of less than
2.7; and a density higher than the density of the first ethylene copolymer, but
15 less than 0.966 g/cm^3 ;

wherein the density of the second ethylene copolymer is less than 0.037 g/cm^3
higher than the density of the first ethylene copolymer; the ratio of
short chain branching in the first ethylene copolymer (SCB1) to the short
chain branching in the second ethylene copolymer (SCB2) is greater than
20 0.5; and wherein the bimodal polyethylene composition has a molecular
weight distribution, M_w/M_n , of from 4.0 to 10.0; a density of from 0.949 to
 0.957 g/cm^3 ; a melt index of from 0.4 to 5.0 g/10 min; a comonomer
content of less than 0.75 mol% as determined by ^{13}C NMR; an Mz of less
than 400,000; a stress exponent of less than 1.50; and an ESCR
25 Condition B (10% IGEPAL) of at least 20 hrs.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 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
5 polyethylene compositions used to manufacture them. The polyethylene compositions are composed of at least two ethylene copolymer components: a first ethylene copolymer and a second ethylene copolymer. 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
10 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 suitably molded aperture, an open necked structure or the like used in combination with a container, a bottle, a jar and the like.

15 The terms “homogeneous” or “homogeneously branched polymer” as used herein define homogeneously branched polyethylene which has a relatively narrow composition distribution, as indicated by a relatively high composition distribution breadth index (CDBI). That is, the comonomer is randomly distributed within a given polymer chain and substantially all of the polymer chains have same
20 ethylene/comonomer ratio.

It is well known that metallocene catalysts and other so called “single site catalysts” incorporate comonomer more evenly than traditional Ziegler-Natta catalysts when used for catalytic ethylene copolymerization with alpha olefins. This fact is often demonstrated by measuring the composition distribution breadth index (CDBI) for
25 corresponding ethylene copolymers. The composition distribution of a polymer can be characterized by the short chain distribution index (SCDI) or composition distribution

breadth index (CDBI). The definition of composition distribution breadth index (CDBI) can be found in U.S. Pat. No. 5,206,075 and PCT publication WO 93/03093. The CDBI is conveniently determined using techniques which isolate polymer fractions based on their solubility (and hence their comonomer content). For example, temperature rising
5 elution fractionation (TREF) as described by Wild et al. J. Poly. Sci., Poly. Phys. Ed. Vol. 20, p441, 1982 or in U.S. Pat. No. 4,798,081 can be employed. From the weight fraction versus composition distribution curve, the CDBI is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median. Generally, Ziegler-
10 Natta catalysts produce ethylene copolymers with a CDBI of less than about 50%, consistent with a heterogeneously branched copolymer. In contrast, metallocenes and other single site catalysts will most often produce ethylene copolymers having a CDBI of greater than about 55%, consistent with a homogeneously branched copolymer.

The First Ethylene Copolymer

15 The first ethylene copolymer of the polyethylene composition of the current invention has a density of from about 0.920 g/cm³ to about 0.955 g/cm³; a melt index, I₂, 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 copolymer. Preferably, the weight average molecular weight, M_w, of
20 the first ethylene copolymer is at least 110,000. Preferably the first ethylene copolymer is a homogeneously branched copolymer.

By the term "ethylene copolymer" it is meant that the copolymer comprises both ethylene and at least one alpha-olefin comonomer.

In an embodiment of the invention, the first ethylene copolymer is made with a
25 single site catalyst, such as for example a phosphinimine catalyst.

The comonomer (i.e. alpha-olefin) content in the first ethylene copolymer can be from about 0.05 to about 3.0 mol%. The comonomer content of the first ethylene polymer is determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples section). The comonomer is one or more
5 suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

The short chain branching in the first ethylene copolymer can be from about 0.25 to about 15 short chain branches per thousand carbon atoms (SCB1/1000Cs). In further embodiments of the invention, the short chain branching in the first ethylene
10 copolymer can be from 0.5 to 15, or from 0.5 to 12, or from 0.5 to 10, or from 0.75 to 15, or from 0.75 to 12, or from 0.75 to 10, or from 1.0 to 10, or from 1.0 to 8.0, or from 1.0 to 5, or from 1.0 to 3 branches per thousand carbon atoms (SCB1/1000Cs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the ethylene copolymer and will for example have two carbon atoms for a 1-butene
15 comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The number of short chain branches in the first ethylene copolymer is determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the
20 like, with 1-octene being preferred.

In an embodiment of the invention, the comonomer content in the first ethylene copolymer is substantially similar or approximately equal (e.g. within about ± 0.05 mol%) to the comonomer content of the second ethylene copolymer (as reported for example in mol%).

In an embodiment of the invention, the comonomer content in the first ethylene copolymer is greater than comonomer content of the second ethylene copolymer (as reported for example in mol%).

In an embodiment of the invention, the amount of short chain branching in the first ethylene copolymer is substantially similar or approximately equal (e.g. within about ± 0.25 SCB/1000Cs) to the amount of short chain branching in the second ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, 1000Cs).

In an embodiment of the invention, the amount of short chain branching in the first ethylene copolymer is greater than the amount of short chain branching in the second ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, 1000Cs).

The melt index of the first ethylene copolymer can in an embodiment of the invention be above 0.01 g/10min, but below 0.4 g/10min.

The density of the first ethylene copolymer is in the present invention from 0.920 to 0.955 g/cm³ or can be a narrower range within this range. For example, in further embodiments of the invention, the density of the first ethylene copolymer can be from 0.925 to 0.955 g/cm³, or from 0.925 to 0.950 g/cm³, or from 0.925 to 0.945 g/cm³, or from 0.925 to 0.940 g/cm³, or from 0.925 to 0.935 g/cm³, or from 0.927 to 0.945 g/cm³, or from 0.927 to 0.940 g/cm³, or from 0.927 to 0.935 g/cm³.

In an embodiment of the invention, the first ethylene copolymer has a molecular weight distribution M_w/M_n of < 3.0, or ≤ 2.7 , or < 2.7, or ≤ 2.5 , or < 2.5, or ≤ 2.3 , or from 1.8 to 2.3.

The density and the melt index, I_2 , of the first ethylene copolymer can be estimated from GPC (gel permeation chromatography) and GPC-FTIR (gel permeation chromatography with Fourier transform infra-red detection) experiments and

deconvolutions carried out on the bimodal polyethylene composition (see the Examples section).

In an embodiment of the invention, the first ethylene copolymer of the polyethylene composition is a homogeneously branched 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 2.7 and a density of from 0.925 to 0.948 g/cm³.

In an embodiment of the present invention, the first ethylene copolymer is homogeneously branched ethylene copolymer and has a CDBI of greater than about 50%, preferably of greater than about 55%. In further embodiments of the invention, the first ethylene copolymer has a CDBI of greater than about 60%, or greater than about 65%, or greater than about 70%.

The first ethylene copolymer can comprise from 10 to 70 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment of the invention, the first ethylene copolymer comprises from 20 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment of the invention, the first ethylene copolymer comprises from 30 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment of the invention, the first ethylene copolymer comprises from 40 to 50 weight percent (wt%) of the total weight of the first and second ethylene copolymers.

The Second Ethylene Copolymer

The second ethylene copolymer of the polyethylene composition of the current invention has a density below 0.967 g/cm³ but which is higher than the density of the first ethylene copolymer; a melt index, I_2 , of from about 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of below about 3.0 and a weight average molecular weight M_w that is less than the M_w of the first ethylene copolymer. Preferably, the weight average molecular weight, M_w of the second ethylene copolymer

will be below 45,000. Preferably the second ethylene copolymer is homogeneously branched copolymer.

By the term "ethylene copolymer" it is meant that the copolymer comprises both ethylene and at least one alpha-olefin comonomer.

5 In an embodiment of the invention, the second ethylene copolymer is made with a single site catalyst, such as for example a phosphinimine catalyst.

The comonomer content in the second ethylene copolymer can be from about 0.05 to about 3 mol% as measured by ^{13}C NMR, or FTIR or GPC-FTIR methods. The comonomer content of the second ethylene polymer can also be determined by
10 mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples 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 the use of 1-octene being preferred.

The short chain branching in the second ethylene copolymer can be from about
15 0.25 to about 15 short chain branches per thousand carbon atoms (SCB2/1000Cs). In further embodiments of the invention, the short chain branching in the second ethylene copolymer can be from 0.25 to 12, or from 0.25 to 8, or from 0.25 to 5, or from 0.25 to 3, or from 0.25 to 2 branches per thousand carbon atoms (SCB2/1000Cs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the
20 ethylene copolymer and will for example have two carbon atoms for a 1-butene comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The number of short chain branches in the second ethylene copolymer can be measured by ^{13}C NMR, or FTIR or GPC-FTIR methods. Alternatively, the number of short chain branches in the second ethylene copolymer can
25 be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples 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.

In an embodiment of the invention, the comonomer content in the second ethylene copolymer is substantially similar or approximately equal (e.g. within about $\pm$ 0.05 mol%) to the comonomer content of the first ethylene copolymer (as reported for example in mol%).

In an embodiment of the invention, the comonomer content in the second ethylene copolymer is less than the comonomer content of the first ethylene copolymer (as reported for example in mol%).

In an embodiment of the invention, the amount of short chain branching in the second ethylene copolymer is substantially similar or approximately equal (e.g. within about $\pm$ 0.25 SCB/1000C) to the amount of short chain branching in the first ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, 1000Cs).

In an embodiment of the invention, the amount of short chain branching in the second ethylene copolymer is less than the amount of short chain branching in the first ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, 1000Cs).

In the present invention, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.967 g/cm³. The density of the second ethylene copolymer in another embodiment of the invention is higher than the density of the first ethylene copolymer but is less than 0.966 g/cm³. In another embodiment of the invention, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.965 g/cm³. In another embodiment of the invention, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.964 g/cm³. In

another embodiment of the invention, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.963 g/cm^3 . In another embodiment of the invention, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.962 g/cm^3 .

5 In an embodiment of the invention, the second ethylene copolymer has a molecular weight distribution M_w/M_n of <3.0 , or ≤ 2.7 , or < 2.7 , or ≤ 2.5 , or < 2.5 , or ≤ 2.3 , or from 1.8 to 2.3.

In an embodiment of the invention, the melt index I_2 of the second ethylene copolymer can be from 20 to 10,000 g/10min. In another embodiment of the invention, 10 the melt index I_2 of the second ethylene copolymer can be from 100 to 10,000 g/10min. In yet another embodiment of the invention, the melt index I_2 of the second ethylene copolymer can be from 1000 to 7000 g/10min. In yet another embodiment of the invention, the melt index I_2 of the second ethylene copolymer can be from 1200 to 10,000 g/10min. In yet another embodiment of the invention, the melt index I_2 of the 15 second ethylene copolymer can be from 1500 to 10,000 g/10min. In yet another embodiment of the invention, the melt index I_2 of the second ethylene copolymer can be greater than 1500, but less than 7000 g/10min.

In an embodiment of the invention, the melt index I_2 of the second ethylene copolymer is greater than 200 g/10min. In an embodiment of the invention, the melt 20 index I_2 of the second ethylene copolymer is greater than 500 g/10min. In an embodiment of the invention, the melt index I_2 of the second ethylene copolymer is greater than 1000 g/10min. In an embodiment of the invention, the melt index I_2 of the second ethylene copolymer is greater than 1200 g/10min. In an embodiment of the invention, the melt index I_2 of the second ethylene copolymer is greater than 1500 25 g/10min.

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

5 The density and the melt index, I_2 , of the second ethylene copolymer can optionally be estimated from GPC and GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition (see the below Examples section).

In an embodiment of the invention, the second ethylene copolymer of 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 2.7 and a density higher than the density of said first ethylene
10 copolymer, but less than 0.967 g/cm³.

In an embodiment of the present invention, the second ethylene copolymer is homogeneously branched ethylene copolymer and has a CDBI of greater than about 50%, preferably of greater than about 55%. In further embodiments of the invention,
15 the second ethylene copolymer has a CDBI of greater than about 60%, or greater than about 65%, or greater than about 70%.

The second ethylene copolymer can comprise from 90 to 30 wt% of the total weight of the first and second ethylene copolymers. In an embodiment of the invention, the second ethylene copolymer comprises from 80 to 40 wt% of the total weight of the
20 first and second ethylene copolymers. In an embodiment of the invention, the second ethylene copolymer comprises from 70 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment of the invention, the second ethylene copolymer comprises from 60 to 50 wt% of the total weight of the first and second ethylene copolymers.

25 In the present invention, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.037 g/cm³

higher than the density of the first ethylene copolymer. In an embodiment of the invention, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.035 g/cm^3 higher than the density of the first ethylene copolymer. In another embodiment of the invention, the second

5 ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.031 g/cm^3 higher than the density of the first ethylene copolymer. In still another embodiment of the invention, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.030 g/cm^3 higher than the density of the first ethylene

10 copolymer.

In embodiments of the invention, the I_2 of the second ethylene copolymer is at least 100 times, or at least 1000 times, or at least 10,000 the I_2 of the first ethylene copolymer.

The Polyethylene Composition

15 The polyethylene composition of this invention has a broad, bimodal or multimodal molecular weight distribution. Minimally, the polyethylene composition will contain a first ethylene copolymer and a second ethylene copolymer (as defined above).

In the present invention, the polyethylene composition will minimally comprise a

20 first ethylene copolymer and a second ethylene copolymer (as defined above) and the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in the first ethylene copolymer (i.e. SCB1) to the number of short chain branches per thousand carbon atoms in the second ethylene copolymer (i.e. SCB2) will be greater than 0.5 (i.e. $\text{SCB1} / \text{SCB2} > 0.5$).

25 In an embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene

copolymer (SCB2) is at least 0.60. In another embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) is at least 0.75. In another embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.0. In yet another embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.25. In still another embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.5.

In an embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) will be greater than 0.5, but less than 1.0.

In an embodiment of the invention, the ratio of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) will be approximately 1.0 (e.g. within $\pm 10\%$, or from about 0.9 to about 1.1).

In embodiments of the invention, the ratio (SCB1/SCB2) of the short chain branching in the first ethylene copolymer (SCB1) to the short chain branching in the second ethylene copolymer (SCB2) will be from 0.75 to 12.0, or from 1.0 to 10, or from 1.0 to 7.0, or from 1.0 to 5.0, or from 1.0 to 3.0.

In a specific embodiment 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 copolymers, where the number of component ethylene copolymers corresponds to the number of discernible
5 peaks. One or more component ethylene copolymers may also exist as a hump, shoulder or tail relative to the molecular weight distribution of the other ethylene copolymer component.

The polyethylene composition of the current invention has a density of greater than or equal to 0.949 g/cm^3 , as measured according to ASTM D792; a melt index, I_2 ,
10 of from about 0.4 to about 5.0 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 11, a Z-average molecular weight, M_z of less than 400,000, a stress exponent of less than 1.50 and an ESCR Condition B at 10% of at least 20 hours.

15 In embodiments of the invention, the polyethylene composition has a comonomer content of less than 0.75 mol%, or less than 0.70 mol%, or less than 0.65 mol%, or less than 0.60 mol%, or less than 0.55 mol% as measured by FTIR or ^{13}C NMR methods, with ^{13}C NMR being preferred, where the comonomer is one or more suitable alpha olefins such as but not limited to 1-butene, 1-hexene, 1-octene and the
20 like, with 1-octene being preferred.

In the present invention, the polyethylene composition has a density of at least 0.949 g/cm^3 . In further embodiments of the invention, the polyethylene composition has a density of or $> 0.949 \text{ g/cm}^3$, or $\geq 0.950 \text{ g/cm}^3$, or $> 0.950 \text{ g/cm}^3$.

In an embodiment of the current invention, the polyethylene composition has a
25 density in the range of from 0.949 to 0.960 g/cm^3 .

In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.949 to 0.959 g/cm³.

In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.949 to 0.957 g/cm³.

5 In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.949 to 0.956 g/cm³.

In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.949 to 0.955 g/cm³.

10 In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.950 to 0.955 g/cm³.

In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.951 to 0.957 g/cm³.

In an embodiment of the current invention, the polyethylene composition has a density in the range of from 0.951 to 0.955 g/cm³.

15 In the current invention, the polyethylene composition has a melt index, I₂, of between 0.4 and 5.0 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight) and including narrower ranges within this range. For example, in further embodiments of the invention, the polyethylene composition has a melt index, I₂, of from 0.5 to 5.0 g/10min, or from 0.4 to 3.5 g/10min, or from 0.4 to 3.0 g/10min, or
20 from 0.5 to 3.5 g/10min, or from 0.5 to 3.0 g/10min, or from 1.0 to 3.0 g/10min, or from about 1.0 to about 2.0 g/10min, or from more than 0.5 to less than 2.0 g/10min.

In an embodiment of the invention, the polyethylene composition has a melt index I₅ of at least 1.0 g/10min according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight). In another embodiment of the invention, the polyethylene
25 composition has a melt index, I₅, 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 further

embodiments of the invention, the polyethylene composition has a melt index I_5 of at least 3.0 g/10min, or at least 4.0 g/10min. In still further embodiments of the invention, the polyethylene composition has a melt index I_5 of from about 1.0 to about 10.0 g/10min, or from about 2.0 to about 8.0 g/10min, or from about 4.0 to about 7.0 g/10min, or from about 3.0 to about 6.5 g/10min.

In an embodiment of the invention, the polyethylene composition has a high load melt index, I_{21} of at least 25 g/10min according to ASTM D1238 (when conducted at 190°C, using a 21 kg weight). In another embodiment of the invention, the polyethylene composition has a high load melt index, I_{21} , of greater than about 50 g/10min. In yet another embodiment of the invention, the polyethylene composition has a high load melt index, I_{21} , of greater than about 75 g/10min. In still another embodiment of the invention, the polyethylene composition has a high load melt index, I_{21} , of greater than about 100 g/10min.

In an embodiment of the invention, the ratio of the melt index, I_2 , of the second ethylene copolymer to the melt index, I_5 , of the polyethylene composition is from 200 to 1500. In another embodiment of the invention, the ratio of the melt index, I_2 , of the second ethylene copolymer to the melt index, I_5 , of the polyethylene composition is from 400 to 1300. In yet another embodiment of the invention, the ratio of the melt index, I_2 , of the second ethylene copolymer to the melt index, I_5 , of the polyethylene composition is from 600 to 1200.

In an embodiment of the invention, the polyethylene composition has a complex viscosity, η^* at a shear stress (G^*) anywhere between from about 1 to about 10 kPa which is between 1,000 to 25,000 Pa.s. In an embodiment of the invention, the polyethylene composition has a complex viscosity, η^* at a shear stress (G^*) anywhere from about 1 to about 10 kPa which is between 1,000 to 10,000 Pa.s.

In an embodiment of the invention, the polyethylene composition has a number average molecular weight, M_n , of below about 30,000. In another embodiment of the invention, the polyethylene composition has a number average molecular weight, M_n , of below about 20,000.

5 In the present invention, the polyethylene composition has a molecular weight distribution M_w/M_n of from 3 to 11 or a narrower range within this range. For example, in further embodiments of the invention, the polyethylene composition has a M_w/M_n of from 4.0 to 10.0, or from 4.0 to 9.0 or from 5.0 to 10.0, or from 5.0 to 9.0, or from 4.5 to 10.0, or from 4.5 to 9.5, or from 4.5 to 9.0, or from 4.5 to 8.5, or from 5.0 to 8.5.

10 In an embodiment of the invention, the polyethylene composition has a ratio of Z-average molecular weight to weight average molecular weight (M_z/M_w) of from 2.25 to 4.5, or from 2.5 to 4.25, or from 2.75 to 4.0, or from 2.75 to 3.75, or between 3.0 and 4.0.

In an embodiment of the invention, the polyethylene composition has a melt flow ratio defined as I_{21}/I_2 of >40 , or ≥ 45 , or ≥ 50 , or ≥ 60 , or ≥ 65 . In a further embodiment of the invention, the polyethylene composition has a melt flow ratio I_{21}/I_2 of from about 40 to about 100, and including narrower ranges within this range. For example, the polyethylene composition may have a melt flow ratio I_{21}/I_2 of from about 45 to about 90, or from about 45 to 80, or from about 45 to 75, or from about 45 to 70, or from about 50 to 90, or from about 50 to 80, or from about 50 to 75, or from about 50 to 70.

In an embodiment of the invention, the polyethylene composition has a melt flow rate defined as I_{21}/I_5 of less than 25. In another embodiment of the invention, the polyethylene composition has a melt flow rate defined as I_{21}/I_5 of less than 20.

In an embodiment of the invention, the polyethylene composition has a shear viscosity at about 10^5 s^{-1} (240°C) of less than about 10 (Pa.s). In further embodiments

of the invention, the polyethylene composition has a shear viscosity at about 10^5s^{-1} (240°C) of less than 7.5 Pa.s, or less than 6.0 Pa.s.

In an embodiment of the invention, the polyethylene composition has a hexane extractables level of below 0.55 wt%.

5 In an embodiment 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 0.75 mol% as determined by ^{13}C NMR. In an embodiment 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 0.65 mol% as determined by ^{13}C NMR. In an
10 embodiment 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 0.55 mol% as determined by ^{13}C NMR.

In an embodiment of the invention, the shear viscosity ratio, $\text{SVR}_{(10,1000)}$ at 240°C of the polyethylene composition can be from about 4.0 to 25, or from 4.0 to 20,
15 or from 4.0 to 17. 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 1000s^{-1} as measured with a capillary rheometer at constant temperature (e.g. 240°C), and a die with L/D ratio of 20 and diameter of 0.06".

In an embodiment of the invention, the shear thinning index, $\text{SHI}_{(1,100)}$ of the
20 polyethylene composition is less than about 10; in another embodiment 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
25 kPa (G^*) and 100 kPa (G^*), respectively.

In an embodiment of the invention, the $SHI_{(1,100)}$ of the polyethylene composition satisfies the equation: $SHI_{(1,100)} < -10.58 (\log I_2 \text{ of polyethylene composition in g/10min}) / (g/10min) + 12.94$. In another embodiment of the invention, the $SHI_{(1,100)}$ of the polyethylene composition satisfies the equation:

5 $SHI_{(1,100)} < -5.5 (\log I_2 \text{ of the polyethylene composition in g/10min}) / (g/10min) + 9.66$.

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

10 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of at least 60 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

15 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of at least 80 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

20 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of at least 120 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

25 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of at least 150 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of from 60 to 400 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

5 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of from 100 to 350 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

10 In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of from 60 to 250 hrs, as measured according to ASTM D1693 (at 10% Igepal and 50°C under condition B).

In an embodiment of the invention, the polyethylene composition or a molded article made from the polyethylene composition has a notched Izod impact strength of
15 at least 60 J/m, as measured according to ASTM D256.

In an embodiment of the invention the polyethylene composition of the current invention has a density of from 0.949 to 0.956 g/cm³; a melt index, I₂, of from 0.5 to 3.0 g/10 min; a molecular weight distribution of from 4.0 to 10.0; a number average molecular weight, M_n, of below 30,000; a shear viscosity at 10⁵s⁻¹ (240°C) of less than
20 10 (Pa.s), a hexane extractables of less than 0.55 %, a notched Izod impact strength of more than 60 J/m, and an ESCR B at 10% of at least 20hrs.

In an embodiment of the invention the polyethylene composition of the current invention has a density of from 0.949 to 0.956 g/cm³; a melt index, I₂, of from 0.5 to 3.0 g/10 min; a molecular weight distribution of from 4.5 to 9.5; a number average
25 molecular weight, M_n, of below 30,000; a shear viscosity at 10⁵s⁻¹ (240°C) of less than 7

(Pa.s), a hexane extractables of less than 0.55 %, a notched Izod impact strength of more than 60 J/m and an ESCR B at 10% of at least 80hrs.

In an embodiment of the invention, the polyethylene composition has a stress exponent, defined as $\text{Log}_{10}[I_6/I_2]/\text{Log}_{10}[6.48/2.16]$, which is ≤ 1.50 . In further

5 embodiments of the invention the polyethylene composition has a stress exponent, $\text{Log}_{10}[I_6/I_2]/\text{Log}_{10}[6.48/2.16]$ of less than 1.50, or less than 1.48, or less than 1.45.

In an embodiment of the invention, the polyethylene composition has a comonomer distribution breadth index (CDBI), as determined by temperature elution fractionation (TREF), of $\geq 60\%$. In further embodiments of the invention, the

10 polyethylene composition will have a CDBI of greater than 65 %, or greater than 70%, or greater than 75%, or greater than 80%.

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

15 perform the mixing of the first ethylene copolymer with the second ethylene copolymer by molten mixing of the two preformed polymers. Preferred are processes in which the first and second ethylene copolymers 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 phase, slurry phase or solution

20 phase reactor systems may be used, with solution phase reactor systems being preferred.

In an embodiment of the current invention, a dual reactor solution process is used as has been described in for example U.S. Pat. No. 6,372,864 and U.S. Pat. Appl. No. 20060247373A1.

25 Homogeneously branched ethylene copolymers 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 phosphinimine catalysts are typically used in combination with activators selected from methylaluminoxanes, boranes or ionic borate salts and are
5 further described in U.S. Pat. Nos 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 3.0 and a
10 composition distribution breadth index (CDBI) of greater than about 50%.

In an embodiment 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 phosphinimine ligand. Such catalysts are known generally as phosphinimine catalysts. Some non-limiting examples of phosphinimine
15 catalysts can be found in U.S. Pat. Nos. 6,342,463; 6,235,672; 6,372,864; 6,984,695; 6,063,879; 6,777,509 and 6,277,931.

Some non-limiting examples of metallocene catalysts can be found in U.S. Pat. Nos. 4,808,561; 4,701,432; 4,937,301; 5,324,800; 5,633,394; 4,935,397; 6,002,033 and 6,489,413. Some non-limiting examples of constrained geometry catalysts can be
20 found in U.S. Pat. Nos. 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,703,187 and 6,034,021 in their entirety.

In an embodiment 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
25 negatively impacting cycle times during the manufacture of caps and closures, such

during the process of compression molding. Long chain branching may be determined using ^{13}C NMR methods and may be quantitatively assessed using the method disclosed by Randall in Rev. Macromol. Chem. Phys. C29 (2 and 3), p. 285.

In an embodiment of the invention, the polyethylene composition will contain
5 fewer than 0.3 long chain branches per 1000 carbon atoms. In another embodiment of the invention, the polyethylene composition will contain fewer than 0.01 long chain branches per 1000 carbon atoms.

In an embodiment of the invention, the polyethylene composition (defined as above) is prepared by contacting ethylene and at least one alpha-olefin with a
10 polymerization catalyst under solution phase polymerization conditions in at least two polymerization reactors (for an example of solution phase polymerization conditions see for example U.S. Pat. No. 6,372,864; 6,984,695 and U.S. App. No. 20060247373A1).

In an embodiment of the invention, the polyethylene composition is prepared by contacting at least one single site polymerization catalyst system (comprising at least
15 one single site catalyst and at least one activator) with ethylene and a least one comonomer (e.g. a C3-C8 alpha-olefin) under solution polymerization conditions in at least two polymerization reactors.

In an embodiment of the invention, a group 4 single site catalyst system, comprising a single site catalyst and an activator, is used in a solution phase dual
20 reactor system to prepare a bimodal polyethylene composition by polymerization of ethylene in the presence of an alpha-olefin comonomer.

In an embodiment of the invention, a group 4 single site catalyst system, comprising a single site catalyst and an activator, is used in a solution phase dual reactor system to prepare a bimodal polyethylene composition by polymerization of
25 ethylene in the presence of 1-octene.

In an embodiment of the invention, a group 4 phosphinimine catalyst system, comprising a phosphinimine catalyst and an activator, is used in a solution phase dual reactor system to prepare a bimodal polyethylene composition by polymerization of ethylene in the presence of an alpha-olefin comonomer.

5 In an embodiment of the invention, a group 4 phosphinimine catalyst system, comprising a phosphinimine catalyst and an activator, is used in a solution phase dual reactor system to prepare a bimodal polyethylene composition by polymerization of ethylene in the presence of 1-octene.

In an embodiment of the invention, a solution phase dual reactor system
10 comprises two solution phase reactors connected in series.

In an embodiment of the invention, a polymerization process to prepare the polyethylene composition comprises contacting at least one single site polymerization catalyst system with ethylene and at least one alpha-olefin comonomer under solution polymerization conditions in at least two polymerization reactors.

15 In an embodiment of the invention, a polymerization process to prepare the polyethylene composition comprises contacting at least one single site polymerization catalyst system with ethylene and at least one alpha-olefin comonomer under solution polymerization conditions in a first reactor and a second reactor configured in series.

In an embodiment of the invention, a polymerization process to prepare the
20 polyethylene composition comprises contacting at least one single site polymerization catalyst system with ethylene and at least one alpha-olefin comonomer under solution polymerization conditions in a first reactor and a second reactor configured in series, with the at least one alpha-olefin comonomer being fed exclusively to the first reactor.

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

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.

5 Optionally, additives can be added to the polyethylene composition. 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
10 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 additives such as erucimide, and nucleating agents (including
15 nucleators, pigments or any other chemicals which may provide a nucleating effect to the polyethylene composition). The additives that can be optionally added are typically added in amount of up to 20 weight percent (wt%).

One or more nucleating agent(s) may be introduced into the polyethylene composition by kneading a mixture of the polymer, usually in powder or pellet form, with
20 the nucleating agent, which may be utilized alone or in the form of a concentrate containing further additives such as stabilizers, pigments, antistatics, UV stabilizers and fillers. It should be a material which is wetted or absorbed by the polymer, which is insoluble in the polymer and of melting point higher than that of the polymer, and it should be homogeneously dispersible in the polymer melt in as fine a form as possible
25 (1 to 10 μm). Compounds known to have a nucleating capacity for polyolefins include salts of aliphatic monobasic or dibasic acids or arylalkyl acids, such as sodium

succinate or aluminum phenylacetate; and alkali metal or aluminum salts of aromatic or alicyclic carboxylic acids such as sodium β -naphthoate. Another compound known to have nucleating capacity is sodium benzoate. The effectiveness of nucleation may be monitored microscopically by observation of the degree of reduction in size of the spherulites into which the crystallites are aggregated.

In an embodiment of the invention, the polymer compositions described above are used in the formation of molded articles. For example, articles formed by compression molding and injection molding are contemplated. Such articles include, for example, caps, 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, injection blow molding, blow molding and sheet extrusion applications.

In an embodiment of the invention, a closure (or cap) is a screw cap for a bottle.

The caps and 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. Hence, in an embodiment of the invention a closure (or cap) comprising the polyethylene composition (defined above) is prepared with a process comprising at least one compression molding step and/or at least one injection molding step.

The caps and closures (including single piece or multi-piece variants) of the invention comprise the polyethylene 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, carbonated soft drinks and other foodstuffs, including but not limited to liquids that are under an appropriate pressure (i.e. carbonated beverages or appropriately pressurized drinkable liquids).

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 using universal calibration
 5 (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: the instrument was first calibrated with indium; after the calibration, a polymer specimen is equilibrated
 10 at 0°C and then the temperature was increased to 200°C at a heating rate of $10^{\circ}\text{C}/\text{min}$; 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 $10^{\circ}\text{C}/\text{min}$ and kept at 0°C for five minutes; the specimen was then heated to 200°C at a heating rate of $10^{\circ}\text{C}/\text{min}$. The DSC T_m , heat of fusion and crystallinity are reported from the 2nd heating cycle.

15 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-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
 20 discussed in Randall, Rev. Macromol. Chem. Phys., C29 (2&3), p 285; U.S. Pat. No. 5,292,845 and WO 2005/121239.

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

Hexane extractables were determined according to ASTM D5227.

25 Shear viscosity was measured by using a Kayeness WinKARS Capillary Rheometer (model # D5052M-115). For the shear viscosity at lower shear rates, a die

having a die diameter of 0.06 inch and L/D ratio of 20 and an entrance angle of 180 degrees was used. For the shear viscosity at higher shear rates, a die having a die diameter of 0.012 inch and L/D ratio of 20 was used.

Melt indexes, I_2 , I_5 , 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 5 kg, a 6.48 kg and a 21 kg weight respectively).

To determine CDBI, a solubility distribution curve is first generated for the polyethylene composition. This is accomplished using data acquired from the TREF technique. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a cumulative distribution curve of weight fraction versus comonomer content, from which the CDBI is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median (See U.S. Pat. No. 5,376,439).

The specific temperature rising elution fractionation (TREF) method used herein was as follows. Polymer samples (50 to 150 mg) were introduced into the reactor vessel of a crystallization-TREF unit (Polymer ChAR™). The reactor vessel was filled with 20 to 40 ml 1,2,4-trichlorobenzene (TCB), and heated to the desired dissolution temperature (e.g. 150 °C) for 1 to 3 hours. The solution (0.5 to 1.5 ml) was then loaded into the TREF column filled with stainless steel beads. After equilibration at a given stabilization temperature (e.g. 110 °C) for 30 to 45 minutes, the polymer solution was allowed to crystallize with a temperature drop from the stabilization temperature to 30°C (0.1 or 0.2 °C/minute). After equilibrating at 30°C for 30 minutes, the crystallized sample was eluted with TCB (0.5 or 0.75 mL/minute) with a temperature ramp from 30°C to the stabilization temperature (0.25 or 1.0 °C/minute). The TREF column was cleaned at the end of the run for 30 minutes at the dissolution temperature. The data

were processed using Polymer ChAR software, Excel spreadsheet and TREF software developed in-house.

The melt index, I_2 and density of the first and second ethylene copolymers were estimated by GPC and GPC-FTIR deconvolutions as discussed further below.

5 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 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
10 distribution function and it has a homogeneous comonomer distribution across the whole molecular weight range.

For these single site catalyzed resins, the GPC data from GPC chromatographs was fit based on Flory's molecular weight distribution function.

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

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

20

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 $M_z = 1.5 \times M_w$ 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 ,

25 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 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 (i.e. the first and second ethylene copolymers) allowed the estimation of the short chain branching content (SCB) from the GPC-FTIR data, in branches per 1000 carbon atoms and calculation of comonomer content (in mol%) and density (in g/cm³) for the first and second ethylene copolymers, based on the deconvoluted relative amounts of first and second ethylene copolymer 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 composition) melt index, I_2 , model was used according to the following equations to calculate the density and melt index I_2 of the first and second ethylene polymers:

$$\begin{aligned} \text{density} = & 0.979863 - 0.00594808 \cdot (\text{FTIR SCB}/1000\text{C})^{0.65} - \\ & 0.000383133 \cdot [\text{Log}_{10}(M_n)]^3 \\ & - 0.00000577986 \cdot (M_w/M_n)^3 + 0.00557395 \cdot (M_z/M_w)^{0.25}; \end{aligned}$$

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

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 GPC deconvolutions.

Hence, these two models were used to estimate the melt indexes and the densities of the components (i.e. the first and second ethylene copolymers).

Plaques molded from the polyethylene compositions were tested according to the following ASTM methods: Bent Strip Environmental Stress Crack Resistance (ESCR) at Condition B at 10% IGEPAL at 50°C, 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.

Dynamic mechanical analyses were carried out with a rheometer, namely Rheometrics Dynamic Spectrometer (RDS-II) or Rheometrics SR5 or ATS Stresstech, on compression molded samples under nitrogen atmosphere at 190°C, using 25 mm diameter cone and plate geometry. The oscillatory shear experiments were done within the linear viscoelastic range of strain (10% strain) at frequencies from 0.05 to 100 rad/s. The values of storage modulus (G'), loss modulus (G''), complex modulus (G^*) and complex viscosity (η^*) were obtained as a function of frequency. The same rheological data can also be obtained by using a 25 mm diameter parallel plate geometry at 190°C under nitrogen atmosphere. The SHI(1,100) value is calculated according to the methods described in WO 2006/048253 and WO 2006/048254.

Examples of the 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 in-series "dual reactor" process produces an "in-situ" polyethylene blend (i.e. the polyethylene composition). Note, that when an in-series reactor configuration is used, un-reacted ethylene monomer, and un-reacted alpha-olefin comonomer present in the first reactor will flow into the downstream second reactor for further polymerization.

In the present inventive examples, although no co-monomer is feed directly to the downstream second reactor, an ethylene copolymer is nevertheless formed in second reactor due to the significant presence of un-reacted 1-octene flowing from the first reactor to the second reactor where it is copolymerized with ethylene. 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 22 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 phosphinimine 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.

The polymerization conditions used to make the inventive compositions are provided in Table 1.

Inventive and comparative polyethylene composition properties are described in Tables 2.

Calculated properties for the first ethylene copolymer and the second ethylene copolymer for selected comparative and inventive polyethylene compositions, as obtained from GPC-FTIR deconvolution studies, are provided in Table 3.

The properties of pressed plaques made from comparative and inventive polyethylene compositions are provided in Table 4.

Comparative polyethylene compositions (Comparative Examples 1-5) are made using a single site phosphinimine catalyst in a dual reactor solution process and have an ESCR at condition B10 of less than 24 hours and a SCB1/SCB2 ratio of 0.50 or less.

Comparative polyethylene composition (Comparative Example 6), is a commercially available resin from Dow Chemical, DMDA-1250 NT 7, and has an ESCR at condition B-10 of more than 150 hours and an Mz of greater than 400,000.

Inventive polyethylene compositions (Inventive Examples 1-9) are made using a
5 single site phosphinimine catalyst in a dual reactor solution process as described above and have an ESCR at condition B10 of greater than 20 hours and a SCB1/SCB2 ratio of greater than 0.50. These inventive examples also have a Mz values of less than 400,000.

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TABLE 1
Reactor Conditions for Inventive Examples

Example No.	Inventive Example 1	Inventive Example 2	Inventive Example 3	Inventive Example 4	Inventive Example 5
Reactor 1					
Ethylene (kg/h)	35.6	38.1	35.7	36.7	37.5
Octene (kg/h)	4.9	4	5.3	4.1	4.8
Hydrogen (g/h)	0.51	0.58	0.51	0.50	0.50
Solvent (kg/h)	319.2	329	296.5	296.8	286.8
Reactor Feed Inlet Temperature (°C)	30	30	30	30	30
Reactor Temperature (°C)	138.2	140.5	141.1	143.8	149.2 ¹⁰
Titanium Catalyst (ppm)	0.14	0.10	0.12	0.1	0.1
Reactor 2					
Ethylene (kg/h)	43.6	51.6	43.6	44.9	45.9
Octene (kg/h)	0	0	0	0	0
Hydrogen (g/h)	22.2	13.46	22.2	16.4	21
Solvent (kg/h)	106.7	137.2	129.1	127.5	135
Reactor Feed Inlet Temperature (°C)	30	30	30	31.3	29.8
Reactor Temperature (°C)	186.9	192.1	186.3	190.9	194
Titanium Catalyst (ppm)	0.29	0.23	0.21	0.21	0.24 ¹⁵

TABLE 1 CONTINUED
Reactor Conditions for Inventive Examples

Example No.	Inventive Example 6	Inventive Example 7	Inventive Example 8	Inventive Example 9
Reactor 1				
Ethylene (kg/h)	35.7	35.6	35.7	38.4
Octene (kg/h)	2.6	4.7	4.9	1.5
Hydrogen (g/h)	0.45	0.46	0.46	0.62
Solvent (kg/h)	256.6	259.1	258.9	346.3
Reactor Feed Inlet Temperature (°C)	30	30	30	30
Reactor Temperature (°C)	152.5	151	147	141.1
Titanium Catalyst (ppm)	0.08	0.13	0.10	0.10
Reactor 2				
Ethylene (kg/h)	43.6	43.6	43.6	51.9
Octene (kg/h)	0	0	0	0
Hydrogen (g/h)	10.2	21.59	16.21	15.07
Solvent (kg/h)	171.6	167	167.1	121.7
Reactor Feed Inlet Temperature (°C)	30	30	30	30
Reactor Temperature (°C)	185.7	186.2	186.4	192.8
Titanium Catalyst (ppm)	0.13	0.22	0.20	0.31

TABLE 2
Resin Properties

Example No.	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Density (g/cm ³)	0.9534	0.9523	0.9526	0.952	0.953
Rheology/Flow Properties					
Melt Index I ₂ (g/10 min)	1.88	0.625	1.42	1.92	0.68
Melt Flow Ratio (I ₂₁ /I ₂)	56.9	51.2	50.5	77.1	73.2
Stress Exponent	1.41	1.38	1.36	1.38	1.38
I ₂₁ (g/10 min)	107	33.1	71.3	146.0	49.8
I ₅ (g/10 min)			4.23		
I ₂₁ /I ₅			16.86		
Shear Viscosity at 10 ⁵ s ⁻¹ (240°C, Pa-s)			5.8		
Shear Viscosity Ratio $\eta(10s^{-1})/\eta(1000s^{-1})$ at 240°C			12.0		
DMA Data (190°C)			$\eta^* = 5832$ Pa*s at G* = 2.099 kPa; $\eta^* = 5591$ Pa*s at G* = 2.795 kPa		
GPC					
M _n	14393	22392	17827	9891	12424
M _w	91663	109626	105289	77319	104353
M _z	325841	299470	282159	245479	327007
Polydispersity Index (M _w /M _n)	6.37	4.9	5.91	7.82	8.4
M _z /M _w	3.55	3.56	2.68	3.17	3.13
Branch Frequency - FTIR (uncorrected for chain end -CH₃)					
Uncorrected SCB/1000C	2.2	2	2.2	3.7	2.5
Uncorrected comonomer content (mol%)	0.4	0.4	0.4	0.7	0.5
Comonomer ID	Octene	octene	octene	octene	octene
Comonomer mol% measured by ¹³C-NMR					
Hexyl+ branches(≥ 4 carbon atoms), mol%	0.3	0.2	0.28		
Slow-CTREF					
CDBI ₅₀ (%)			63		
DSC					
Primary Melting Peak (°C)	128.3	129.7	129.11	126.8	128.42
Heat of Fusion (J/g)	204.7	198.2	207.7	200.3	213.80
Crystallinity (%)	70.58	68.34	71.61	69.08	73.72
Other properties					
Hexane Extractables (wt%)	0.44	0.46	0.32	0.73	0.57
VICAT Soft. Pt. (°C) - Plaque	126	127	127.3	122	125

Heat Deflection Temp. [C] @ 66 PSI	72	71	68.2	68	71
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TABLE 2 CONTINUED
Resin Properties

Example No.	Comparative Example 6	Inventive Example 1	Inventive Example 2	Inventive Example 3	Inventive Example 4
Density (g/cm ³)	0.955	0.9529	0.9524	0.9524	0.9523
Rheology/Flow Properties					
Melt Index I ₂ (g/10 min)	1.5	1.57	2.94	1.69	1.5
Melt Flow Ratio (I ₂₁ /I ₂)	66	58	44.1	61	54.8
Stress Exponent	1.58	1.38	1.36	1.38	1.4
I ₂₁ (g/10 min)	99	90	129	104	82.3
I ₅ (g/10 min)	5.31	4.72		4.94	4.5
I ₂₁ /I ₅	18.64	19.07		21.05	18.29
Shear Viscosity at 10 ⁵ s ⁻¹ (240°C, Pa-s)	6.2	5.1	6.2	4.8	5.8
Shear Viscosity Ratio $\eta(10s^{-1})/\eta(1000s^{-1})$ at 240°C	11.3	13.5	8.1	13.0	14.8
DMA Data (190°C)		$\eta^* = 5294$ Pa*s at G* = 2.647 kPa; $\eta^* = 5106$ Pa*s at G* = 3.547 kPa		$\eta^* = 4889$ Pa*s at G* = 2.445 kPa; $\eta^* = 4739$ Pa*s at G* = 3.292 kPa	
GPC					
M _n	10240	10524	15679	10579	13309
M _w	106992	83712	74090	86319	88295
M _z	533971	256210	215369	291056	278141
Polydispersity Index (M _w /M _n)	10.45	7.95	4.73	8.16	6.63
M _z /M _w	4.99	3.06	2.91	3.37	3.15
Branch Frequency - FTIR (uncorrected for chain end -CH₃)					
Uncorrected SCB/1000C	2.3	3	1.8	3	2.1
Uncorrected comonomer content (mol%)	0.5	0.6	0.4	0.6	0.4
Comonomer ID	hexene	octene	octene	octene	octene
Comonomer mol% measured by ¹³C-NMR					
Hexyl+ branches(≥ 4 carbon atoms), mol%		0.4		0.4	0.3
Slow-CTREF					
CDBI ₅₀ (%)	63.4	81.8	86.2	80.4	76.5
DSC					
Primary Melting Peak (°C)	130.06	127.3	128.8	127.5	129
Heat of Fusion (J/g)	217.4	203.8	206.1	207.3	209
Crystallinity (%)	74.98	70.27	71.08	71.48	72.08
Other properties					
Hexane Extractables (wt%)	0.36	0.36	0.22	0.42	0.25

VICAT Soft. Pt. (°C) – Plaque	126.8	125.2	126.8	124.8	126.4
Heat Deflection Temp. [C] @ 66 PSI	73	68	74.1	76	67.3

TABLE 2 CONTINUED
Resin Properties

Example No.	Inventive Example 5	Inventive Example 6	Inventive Example 7	Inventive Example 8	Inventive Example 9
Density (g/cm ³)	0.9532	0.9527	0.9534	0.9522	0.9568
Rheology/Flow Properties					
Melt Index I ₂ (g/10 min)	1.78	1.29	2.05	1.31	1.68
Melt Flow Ratio (I ₂₁ /I ₂)	55.6	44.1	55	64	54.2
Stress Exponent	1.37	1.35	1.34	1.39	1.40
I ₂₁ (g/10 min)	99.1	57	113	83	91
I ₅ (g/10 min)	5.33		6.21		
I ₂₁ /I ₅	18.59		18.20		
Shear Viscosity at 10 ⁵ s ⁻¹ (240°C, Pa·s)	5.1	6.3	5.0	5.8	6.0
Shear Viscosity Ratio η(10s ⁻¹)/η(1000s ⁻¹) at 240°C	13.3	11.6	12.1	14.8	11.2
DMA Data (190°C)		η* = 6707 Pa·s at G* = 2.413 kPa; η* = 6465 Pa·s at G* = 3.232 kPa		η* = 6688 Pa·s at G* = 2.407 kPa; η* = 6472 Pa·s at G* = 3.236 kPa	
GPC					
M _n	9716	18449	11145	14021	15110
M _w	84943	93080	80630	93175	85227
M _z	288665	272788	243944	303823	287035
Polydispersity Index (M _w /M _n)	8.74	5.05	7.23	6.65	5.64
M _z /M _w	3.40	2.93	3.03	3.26	3.37
Branch Frequency - FTIR (uncorrected for chain end -CH₃)					
Uncorrected SCB/1000C	2.5	1.7	2.8	2.2	1.3
Uncorrected comonomer content (mol%)	0.5	0.3	0.6	0.4	0.3
Comonomer ID	Octene	octene	octene	octene	octene
Comonomer mol% measured by ¹³C- NMR					
Hexyl+ branches(>= 4 carbon atoms), mol%					
Slow-CTREF					
CDBI ₅₀ (%)	75.2	86.2	79.7	80.4	77.8
DSC					
Primary Melting Peak (°C)	128.3	129.8	127.9	128.4	130.7

Heat of Fusion (J/g)	207.3	208.5	211.1	205.4	213.8
Crystallinity (%)	71.48	71.9	72.8	70.82	73.73
Other properties					
Hexane Extractables (wt%)	0.33	0.25	0.38	0.27	0.24
VICAT Soft. Pt. (°C) – Plaque	125.4	128.2	125.2	126.2	128.4
Heat Deflection Temp. [C] @ 66 PSI	69.8	68.2	66.8	69	77.6

TABLE 3
Polyethylene Component Properties

Example No.	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Inventive Example 3	Inventive Example 4	Inventive Example 5	Inventive Example 7
Density (g/cm ³)	0.9534	0.9523	0.9526	0.952	0.953	0.9524	0.9523	0.9532	0.9534
I ₂ (g/10min.)	1.88	0.625	1.42	1.92	0.68	1.69	1.5	1.78	2.05
Stress Exponent	1.41	1.38	1.36	1.38	1.38	1.38	1.4	1.37	1.34
MFR (I ₂ /I ₂)	56.9	51.2	50.5	77.1	73.2	61	54.8	55.6	55
Mw/Mn	6.37	4.9	6.34	7.82	8.39	8.16	6.63	8.74	7.23
1st Ethylene Copolymer									
weight %	0.43	0.43	0.433	0.426	0.449	0.455	0.454	0.454	0.453
Mw	162400	214300	176200	169500	213200	165100	168100	162700	157200
I ₂ (g/10min.)	0.13	0.05	0.10	0.11	0.05	0.13	0.12	0.13	0.15
Density 1, d1 (g/cm ³)	0.9389	0.9356	0.9334	0.9382	0.9363	0.9325	0.9302	0.9322	0.9316
SCB1 per 1000Cs	0.15	0.13	1.07	0.18	0.06	1.57	2.24	1.71	2.02
mol % octene	0.03	0.03	0.21	0.04	0.01	0.31	0.45	0.34	0.40
2nd Ethylene Copolymer									
weight %	0.57	0.57	0.567	0.574	0.551	0.545	0.546	0.546	0.547
Mw	18500	25600	17300	11700	14300	11100	14900	12100	11400
I ₂ (g/10min.)	736	190	979	5082	2148	6318	1817	4419	5739
Density 2, d2 (g/cm ³)	0.9559	0.9522	0.9528	0.9559	0.9565	0.9614	0.9555	0.959	0.9577
SCB2 per 1000Cs	1.06	1.37	2.16	2.1	1.42	0.63	1.64	1.08	1.59
mol % octene	0.21	0.27	0.43	0.42	0.28	0.13	0.33	0.22	0.32
Estimated (d2 - d1), g/cm ³	0.017	0.0166	0.0194	0.0177	0.0202	0.0289	0.0253	0.0268	0.0261
Estimated (SCB2 - SCB1)	0.91	1.24	1.09	1.92	1.36	-0.94	-0.6	-0.63	-0.43
SCB1/SCB2	0.14	0.09	0.50	0.09	0.04	2.5	1.37	1.58	1.27

TABLE 4
Plaque Properties

Example No.	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Environmental Stress Crack Resistance					
ESCR Cond. B at 10 % (hrs)	<24	<24	< 24	<24	< 24
Flexural Properties (Plaques)					
Flex Secant Mod. 1% (MPa)	1035	1070	1198	1062	1201
Flex Sec Mod 1% (MPa) Dev.	25	37	38	34	41
Flex Secant Mod. 2% (MPa)	877	906	1011	904	1002
Flex Sec Mod 2% (MPa) Dev.	19	29	22	28	32
Flexural Strength (MPa)	31.5	33.4	35.1	33	35.5
Flexural Strength Dev. (MPa)	0.6	0.7	0.4	0.9	0.6
Tensile Properties (Plaques)					
Elong. at Yield (%)	10.2	10.3	10	10.3	10.2
Elong. at Yield Dev. (%)	0.8	1	0	0.3	0.4
Yield Strength (MPa)	26.6	25.4	26.3	25.7	26.9
Yield Strength Dev. (MPa)	0.3	0.4	0.6	0.6	0.3
Ultimate Elong. (%)	920	1003	858	535	800
Ultimate Elong.Dev. (%)	94.6	23.7	37	167.4	86.1
Ultimate Strength (MPa)	21.5	33.8	21.4	14.8	20.7
Ultimate Strength Dev. (MPa)	4.1	1.1	1.8	0.7	6.7
Sec Mod 1% (MPa)	1374	1138	1294	1244	1237
Sec Mod 1% (MPa) Dev.	276.4	210.8	188	47.1	83
Sec Mod 2% (MPa)	937	834	900	858	888
Sec Mod 2% (MPa) Dev.	71	61	44	24	47
Impact Properties (Plaques)					
Notched Izod Impact (J/m)	76	139	64.1	69.4	97.1
IZOD DV (J/m)	7	7	5.3	6.9	2.8

TABLE 4 CONTINUED
Plaque Properties

Example No.	Comparative Example 6	Inventive Example 1	Inventive Example 2	Inventive Example 3	Inventive Example 4
Environmental Stress Crack Resistance					
ESCR Cond. B at 10 % (hrs)	196	309	23	212	86
Flexural Properties (Plaques)					
Flex Secant Mod. 1% (MPa)	1372	1274	1247	1267	1295
Flex Sec Mod 1% (MPa) Dev.	87	39	44	19	23
Flex Secant Mod. 2% (MPa)	1167	1064	1035	1060	1085
Flex Sec Mod 2% (MPa) Dev.	45	29	33	14	21
Flexural Strength (MPa)	40.4	37.5	36.7	37.1	37.3
Flexural Strength Dev. (MPa)	1	0.8	0.4	0.3	0.4
Tensile Properties (Plaques)					
Elong. at Yield (%)	9	9	10	8	10
Elong. at Yield Dev. (%)	1	1	1	0	0
Yield Strength (MPa)	28.5	26	25.6	26.4	26.3
Yield Strength Dev. (MPa)	0.3	0.2	0.1	0.3	0.3
Ultimate Elong. (%)	870	701	988	762	891
Ultimate Elong. Dev. (%)	69	106	58	98	23
Ultimate Strength (MPa)	26.8	21.8	32.2	24.7	33.3
Ultimate Strength Dev. (MPa)	5.5	6.8	1.9	7.4	2
Sec Mod 1% (MPa)	1696	1483	1256	1331	1230
Sec Mod 1% (MPa) Dev.	279	121	333	241	90
Sec Mod 2% (MPa)	1118	973	880	939	913
Sec Mod 2% (MPa) Dev.	90	33	88	62	34
Impact Properties (Plaques)					
Notched Izod Impact (J/m)	80.1	74.7	69.4	69.4	80.1
IZOD DV (J/m)	5.3	0.0	0.0	0.0	2.7

TABLE 4 CONTINUED
Plaque Properties

Example No.	Inventive Example 5	Inventive Example 6	Inventive Example 7	Inventive Example 8	Inventive Example 9
Environmental Stress Crack Resistance					
ESCR Cond. B at 10 % (hrs)	83	60	73	157	24
Flexural Properties (Plaques)					
Flex Secant Mod. 1% (MPa)	1304	1240	1318	1260	1402
Flex Sec Mod 1% (MPa) Dev.	57	31	37	25	48
Flex Secant Mod. 2% (MPa)	1092	1026	1098	1049	1159
Flex Sec Mod 2% (MPa) Dev.	40	26	24	15	35
Flexural Strength (MPa)	37.6	36.1	38.2	36.9	39.8
Flexural Strength Dev. (MPa)	0.8	0.6	0.3	0.6	1.1
Tensile Properties (Plaques)					
Elong. at Yield (%)	9	10	8	9	10
Elong. at Yield Dev. (%)	0	0	0	1	0
Yield Strength (MPa)	26.4	25.6	26.9	26.1	28.2
Yield Strength Dev. (MPa)	0.2	0.2	0.2	0.2	0.6
Ultimate Elong. (%)	862	974	766	836	923
Ultimate Elong.Dev. (%)	47	35	130	103	104
Ultimate Strength (MPa)	29.7	36.3	22.9	29.6	26.9
Ultimate Strength Dev. (MPa)	2.7	1.5	7	5.5	6.9
Sec Mod 1% (MPa)	1197	1333	1429	1395	1367
Sec Mod 1% (MPa) Dev.	128	213	183	217	190
Sec Mod 2% (MPa)	881	893	979	934	966
Sec Mod 2% (MPa) Dev.	40	70	52	73	67
Impact Properties (Plaques)					
Notched Izod Impact (J/m)	64.1	128.1	64.1	80.1	90.7
IZOD DV (J/m)	2.1	5.3	0.0	0.0	5.3

As can be seen from the data provided in Tables 2, 3 and 4, the Inventive polyethylene compositions (Inventive Examples 1-9) which have a ratio of short chain branching SCB1/SCB2 of greater than 0.5, have improved ESCR B properties while maintaining good processability.

5 Shear Thinning Index

As shown in Figure 1, the inventive polyethylene compositions 1, 3, 5, 6 and 8 do not satisfy the equation $SHI_{(1, 100)} \geq -10.58 (\log I_2 \text{ of the polyethylene composition in g/10min}) / (g/10min) + 12.94$, which is a property of the blends taught in WO 2006/048253. As shown in Figure 1, the inventive polyethylene compositions 1, 3, 5, 6 and 8 do not satisfy the equation:

$SHI_{(1, 100)} \geq -5.5 (\log I_2 \text{ of the polyethylene composition in g/10min}) / (g/10min) + 9.66$, which is a property of the blends taught in and WO 2006/048254.

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

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

- (1) 10 to 70 wt% of a first ethylene copolymer 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; and a density of from 0.920 to 0.955 g/cm³; and
- (2) 90 to 30 wt% of a second ethylene copolymer having a melt index I_2 , of from 100 to 10,000 g/10min; a molecular weight distribution M_w/M_n , of less than 3.0; and a density higher than the density of said first ethylene copolymer, but less than 0.967 g/cm³;

wherein the density of said second ethylene copolymer is less than 0.037 g/cm³ higher than the density of said first ethylene copolymer; the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is greater than 0.5; and wherein said bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 3 to 11; a density of at least 0.949 g/cm³; a melt index, I_2 of from 0.4 to 5.0 g/10 min; an M_z of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAL) of at least 20 hrs.

2. The closure of claim 1 wherein the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1)

to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is at least 1.0.

3. The closure of claim 1 wherein the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is at least 1.5.

4. The closure of claim 1 wherein said bimodal polyethylene composition has an ESCR Condition B (10% IGEPAL) of at least 60 hrs.

5. The closure of claim 1 wherein said bimodal polyethylene composition has an ESCR Condition B (10% IGEPAL) of at least 120 hrs.

6. The closure of claim 1 wherein said bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 4.5 to 9.5.

7. The closure of claim 1 wherein said bimodal polyethylene composition has melt index, I_2 , of from 0.4 to 3.0 g/10min.

8. The closure of claim 1 wherein said first ethylene copolymer has a density of from 0.925 to 0.950 g/cm³.

9. The closure of claim 1 wherein said second ethylene copolymer has a density of less than 0.965 g/cm³.

10. The closure of claim 1 wherein said bimodal polyethylene composition has a density of from 0.951 to 0.957 g/cm³.
11. The closure of claim 1 wherein the density of said second ethylene copolymer is less than 0.031 g/cm³ higher than the density of said first ethylene copolymer.
12. The closure of claim 1 wherein said second ethylene copolymer has a melt index I₂, of greater than 1500 g/10min.
13. The closure of claim 1 wherein said first and second ethylene copolymers have a M_w/M_n of less than 2.5.
14. The closure of claim 1 wherein said bimodal polyethylene composition has a comonomer distribution breadth index (CDBI) of greater than 65%.
15. The closure of claim 1 wherein said bimodal polyethylene composition comprises:
 - from 30 to 60 wt% of said first ethylene copolymer; and
 - from 70 to 40 wt% of said second ethylene copolymer.
16. The closure of claim 1 wherein said bimodal polyethylene composition has a comonomer content of less than 0.75 mol% as determined by ¹³C NMR.

17. The closure of claim 1 wherein the bimodal polyethylene composition further comprises a nucleating agent.
18. The closure of claim 1 wherein said first and second ethylene copolymers are copolymers of ethylene and 1-octene.
19. The closure of claim 1 wherein said closure is made by compression molding or injection molding.
20. The closure of claim 1 wherein said closure is a screw cap.
21. The closure of claim 1 wherein said bimodal polyethylene composition is prepared by contacting ethylene and an alpha-olefin with a polymerization catalyst under solution polymerization conditions in at least two polymerization reactors.
22. A process to prepare a polyethylene composition, said polyethylene composition comprising:
- (1) 10 to 70 wt% of a first ethylene copolymer 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; and a density of from 0.920 to 0.955 g/cm³; and
 - (2) 90 to 30 wt% of a second ethylene copolymer having a melt index I_2 , of from 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of less than 3.0; and a density higher than the density of said first ethylene copolymer, but less than 0.967 g/cm³;

wherein the density of said second ethylene copolymer is less than 0.037 g/cm³ higher than the density of said first ethylene copolymer; the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is greater than 0.5; and wherein said bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 3 to 11; a density of at least 0.949 g/cm³; a melt index, I_2 of from 0.4 to 5.0 g/10 min; an M_z of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAL) of at least 20 hrs;

said process comprising contacting at least one single site polymerization catalyst system with ethylene and at least one alpha-olefin under solution polymerization conditions in at least two polymerization reactors.

23. The process of claim 22 wherein said at least two polymerization reactors comprise a first reactor and a second reactor configured in series.

24. The process of claim 23 wherein said at least one alpha-olefin is fed exclusively to said first reactor.

25. A bimodal polyethylene composition comprising:

- (1) 30 to 60 wt% of a first ethylene copolymer having a melt index, I_2 , of less than 0.4 g/10min; a molecular weight distribution, M_w/M_n , of less than 2.7; and a density of from 0.925 to 0.950 g/cm³; and
- (2) 70 to 40 wt% of a second ethylene copolymer having a melt index I_2 , of from 100 to 10,000 g/10min; a molecular weight distribution, M_w/M_n , of less than 2.7; and a density higher than the density of said first ethylene copolymer, but less than 0.966 g/cm³;

wherein the density of said second ethylene copolymer is less than 0.037 g/cm³ higher than the density of said first ethylene copolymer; the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is greater than 0.5; and wherein said bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 4.0 to 10.0; a density of from 0.949 to 0.957 g/cm³; a melt index, I_2 of from 0.4 to 5.0 g/10 min; a comonomer content of less than 0.75 mol% as determined by ¹³C NMR; an M_z of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAI) of at least 20 hrs.

26. The bimodal polyethylene composition of claim 25 wherein said bimodal polyethylene composition has melt index I_2 , of from 0.5 to 3.0 g/10min.

27. The bimodal polyethylene composition of claim 25 wherein said first ethylene copolymer has a density of from 0.925 to 0.945 g/cm³.

28. The bimodal polyethylene composition of claim 25 wherein said second ethylene copolymer has a density of less than 0.965 g/cm³.
29. The bimodal polyethylene composition of claim 25 wherein said bimodal polyethylene composition has a density of from 0.951 to 0.957 g/cm³.
30. The bimodal polyethylene composition of claim 25 wherein the density of said second ethylene copolymer is less than 0.031 g/cm³ higher than the density of said first ethylene copolymer.
31. The bimodal polyethylene composition of claim 25 wherein said bimodal polyethylene composition has a molecular weight distribution, M_w/M_n , of from 4.5 to 9.0.
32. The bimodal polyethylene composition of claim 25 wherein the ratio (SCB1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is at least 1.0.
33. The bimodal polyethylene composition of claim 25 wherein said bimodal polyethylene composition has an ESCR Condition B (10% IGEPAL) of at least 60 hrs.

FIGURE 1

