

ETHYLENE-BASED POLYMER COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 61/222,371, filed July 1, 2009, and fully incorporated herein by reference.

FIELD OF INVENTION

The instant invention relates to an ethylene-based polymer composition, and the method for producing the same.

BACKGROUND OF THE INVENTION

There have been many varieties of polyethylene polymers polymerized over the years, including those made using high pressure free radical chemistry (LDPE), more traditional linear low-density polyethylene (LLDPE) typically made using Ziegler-Natta catalysis and metallocene or constrained geometry catalyzed polyethylene, some linear polyethylenes, but also some substantially linear polyethylene containing slight amount of long chain branching. While these polymers have varying positives and negatives, depending on application or end-use, more control over the polymer structure is still desired.

We have now found that post-metallocene catalysts can efficiently polymerize ethylene into polymers and polymer compositions having controlled comonomer distribution profiles, while also controlling unsaturation levels in the polymer.

BRIEF SUMMARY

The instant disclosure provides an ethylene-based polymer composition, and the method for producing the same. In one aspect, there is provided an ethylene-based polymer composition characterized by a Comonomer Distribution Constant in the range of from greater than 45 to less than 400, wherein the composition has less than 120 total unsaturation unit/1,000,000C. In one embodiment, the Comonomer Distribution Constant may be greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200. Preferably, the inventive ethylene-based polymer compositions comprise up to about 3 long chain branches/1000 carbons, more preferably from about 0.01 to about 3 long chain branches/1000 carbons. The inventive ethylene-based polymer compositions can have a ZSVR of at least 2. The inventive ethylene-based polymer compositions can be further characterized by comprising less than 20

vinylidene unsaturation unit/1,000,000C. The inventive ethylene-based polymer compositions can have a bimodal molecular weight distribution (MWD) or a multi-modal MWD. The inventive ethylene-based polymer compositions can have a comonomer distribution profile comprising a mono or bimodal distribution in the temperature range of from 35°C to 120°C, excluding purge. The inventive ethylene-based polymer compositions can comprise a single DSC melting peak. The inventive ethylene-based polymer compositions can comprise a weight average molecular weight (Mw) from about 17,000 to about 220,000.

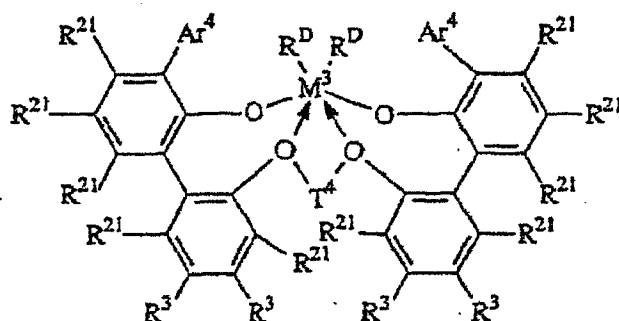
In another aspect, there is provided a fabricated article comprising the composition as defined above. This may be especially in the form of at least one film layer. In another aspect, there is provided a thermoplastic formulation comprising the composition as defined above and at least one natural or synthetic polymer.

The inventive ethylene-based polymer compositions can be at least partially cross-linked (at least 5% (weight) gel).

In another aspect, there is provided a polymerization process comprising:

(A) polymerizing ethylene and optionally one or more α -olefins in the presence of a first catalyst to form a semi-crystalline ethylene-based polymer in a first reactor or a first part of a multi-part reactor; and

(B) reacting freshly supplied ethylene and optionally one or more α -olefins in the presence of a second catalyst comprising an organometallic catalyst thereby forming an ethylene-based polymer composition as defined above in at least one other reactor or a later part of said multi-part reactor, wherein the catalyst of (A) and (B) can be the same or different and each is a metal complex of a polyvalent aryloxyether corresponding to the formula:



where M^3 is Ti, Hf or Zr, preferably Zr;

Ar^4 is independently in each occurrence a substituted C_{9-20} aryl group, wherein the substituents, independently in each occurrence, are selected from the group consisting of

alkyl; cycloalkyl; and aryl groups; and halo-, trihydrocarbylsilyl- and halohydrocarbyl-substituted derivatives thereof, with the proviso that at least one substituent lacks co-planarity with the aryl group to which it is attached;

5 T^4 is independently in each occurrence a C_{2-20} alkylene, cycloalkylene or cycloalkenylene group, or an inertly substituted derivative thereof;

R^{21} is independently in each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or di(hydrocarbyl)amino group of up to 50 atoms not counting hydrogen;

10 R^3 is independently in each occurrence hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen, or two R^3 groups on the same arylene ring together or an R^3 and an R^{21} group on the same or different arylene ring together form a divalent ligand group attached to the arylene group in two positions or join two different arylene rings together; and

15 R^D is independently in each occurrence halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl, diene, or poly(hydrocarbyl)silylene group.

In yet another embodiment, the present disclosure is a method of characterizing an ethylene based polymer for comonomer composition distribution (CDC), wherein CDC is calculated from comonomer distribution profile by CEF, and CDC is defined as Comonomer
20 Distribution Index divided by Comonomer Distribution Shape Factor multiplying by 100 as shown in Equation 1, Figure 1, and wherein Comonomer distribution index stands for the total weight fraction of polymer chains with the comonomer content ranging from 0.5 of median comonomer content (C_{median}) and 1.5 of C_{median} from 35.0 to 119.0°C, and wherein Comonomer Distribution Shape Factor is defined as a ratio of the half width of comonomer
25 distribution profile divided by the standard deviation of comonomer distribution profile from the peak temperature (T_p), and wherein the method comprises the following steps:

(A) Obtain a weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step increase of 0.200°C from CEF according to Equation 2, as shown in
30 Figure 2;

(B) Calculate the median temperature (T_{median}) at cumulative weight fraction of 0.500, according to Equation 3, as shown in Figure 3;

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(C) Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve according to Equation 4, as shown in Figure 4;

(D) Construct a comonomer content calibration curve by using a series of reference materials with known amount of comonomer content, i.e., eleven reference materials with narrow comonomer distribution (mono-modal comonomer distribution in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (measured via conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0 mole% are analyzed with CEF at the same experimental conditions specified in CEF experimental sections;

(E) Calculate comonomer content calibration by using the peak temperature (T_p) of each reference material and its comonomer content; The calibration is calculated from each reference material as shown in Formula 4, Figure 4, wherein: R^2 is the correlation constant;

(F) Calculate Comonomer Distribution Index from the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$, and if T_{median} is higher than 98.0°C, Comonomer Distribution Index is defined as 0.95;

(G) Obtain Maximum peak height from CEF comonomer distribution profile by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two peaks are identical, then the lower temperature peak is selected); half width is defined as the temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched forward from 35.0°C, while the rear temperature at the half of the maximum peak is searched backward from 119.0°C, in the case of a well defined bimodal distribution where the difference in the peak temperatures is equal to or greater than the 1.1 times of the sum of half width of each peak, the half width of the inventive ethylene-based polymer composition is calculated as the arithmetic average of the half width of each peak;

(H) Calculate the standard deviation of temperature ($Stdev$) according Equation 5, as shown in Figure 5.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of illustrating the invention, there is shown in the drawings a form that is exemplary; it being understood, however, that this invention is not limited to the precise arrangements and illustrations shown.

Figs. 1-18 illustrate Formulas 1-18, respectively;

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Fig. 19 is a graphical illustration of CDC calculation obtaining peak temperature, half width and median temperature from CEF, showing comonomer distribution profile of Example 3;

Fig. 20 is a graph illustrating integration limits for unsaturation for Example 3, the dash line means the position can be slightly different depends on the sample/catalyst;

Fig. 21 illustrates the modified pulse sequences for unsaturation with Bruker AVANCE 400 MHz spectrometer;

Fig. 22 illustrates chemical structure representations of unsaturations; and

Fig. 23 is a graph illustrating the CEF overlays.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention provides an ethylene-based polymer composition, and the method for producing the same. The inventive ethylene-based polymer composition according to the present inventions is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C. Preferably, the inventive ethylene-based polymer compositions comprise up to about 3 long chain branches/1000 carbons, more preferably from about 0.01 to about 3 long chain branches/1000 carbons. The inventive ethylene-based polymer compositions can have a ZSVR of at least 2. The inventive ethylene-based polymer compositions can be further characterized by comprising less than 20 vinylidene unsaturation unit/1,000,000C. The inventive ethylene-based polymer compositions can have a bimodal molecular weight distribution (MWD) or a multi-modal MWD. The inventive ethylene-based polymer compositions can have a comonomer distribution profile comprising a mono or bimodal distribution in the temperature range of from 35°C to 120°C, excluding purge. The inventive ethylene-based polymer compositions can comprise a single DSC melting peak. The inventive ethylene-based polymer compositions can comprise a weight average molecular weight (Mw) from about 17,000 to about 220,000.

The inventive ethylene-based polymer compositions are made using a metal complex of a polyvalent aryloxyether.

In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably

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greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the composition has less than 120 total unsaturation unit/1,000,000C.

5 In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition comprises up to about 3 long chain branches/1000 carbons, preferably from about 0.01 to about 3 long chain branches/1000 carbons.

10 In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer
15 composition has a ZSVR of at least 2, and optionally the inventive ethylene-based polymer composition is characterized by comprising less than 20 vinylidene unsaturation unit/1,000,000C.

In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably
20 greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition has a bimodal molecular weight distribution (MWD).

In one embodiment, the inventive ethylene-based polymer composition is
25 characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition has a multi-modal MWD.

30 In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total

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unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition has a single DSC melting peak.

In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition has been at least partially cross-linked (at least 5% gel).

In one embodiment, the inventive ethylene-based polymer composition is characterized by a Comonomer Distribution Constant greater than about 45, more preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the inventive ethylene-based polymer composition has less than 120 total unsaturation unit/1,000,000C, and wherein the inventive ethylene-based polymer composition has a comonomer distribution profile comprising a mono or bimodal distribution in the temperature range of from 35°C to 120°C, excluding purge.

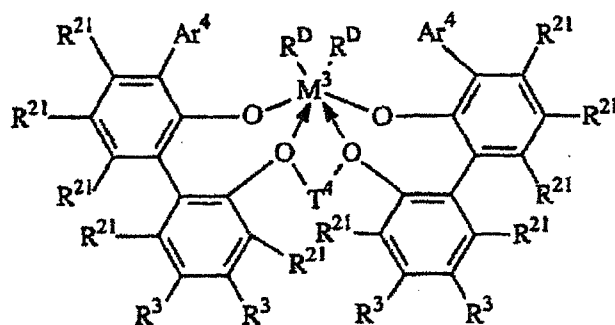
The present invention further provides a thermoplastic formulation comprising the inventive ethylene-based polymer composition, as described herein, and at least one natural or synthetic polymer.

The present invention further provides a fabricated article comprising the inventive ethylene-based polymer composition, as described herein.

In another embodiment, the invention is a process comprising:

- (A) polymerizing ethylene and optionally one or more α -olefins in the presence of a first catalyst to form a semi-crystalline ethylene-based polymer in a first reactor or a first part of a multi-part reactor; and
- (B) reacting freshly supplied ethylene and optionally one or more α -olefins in the presence of a second catalyst comprising an organometallic catalyst thereby forming an ethylene-based polymer composition in at least one other reactor or a later part of a multi-part reactor, wherein the catalyst of (A) and (B) can be the same or different and each is a metal complex of a polyvalent aryloxyether corresponding to the formula:

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wherein M^3 is Ti, Hf or Zr, preferably Zr;

Ar^4 is independently in each occurrence a substituted C_{9-20} aryl group, wherein the substituents, independently in each occurrence, are selected from the group consisting of alkyl; cycloalkyl; and aryl groups; and halo-, trihydrocarbylsilyl- and halohydrocarbyl-substituted derivatives thereof, with the proviso that at least one substituent lacks co-planarity with the aryl group to which it is attached;

T^4 is independently in each occurrence a C_{2-20} alkylene, cycloalkylene or cycloalkenylene group, or an inertly substituted derivative thereof;

R^{21} is independently in each occurrence hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or di(hydrocarbyl)amino group of up to 50 atoms not counting hydrogen;

R^3 is independently in each occurrence hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen, or two R^3 groups on the same arylene ring together or an R^3 and an R^{21} group on the same or different arylene ring together form a divalent ligand group attached to the arylene group in two positions or join two different arylene rings together; and

R^D is independently in each occurrence halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl, diene, or poly(hydrocarbyl)silylene group.

In yet another embodiment, the present invention is a method of characterizing an ethylene based polymer for comonomer composition distribution (CDC), wherein CDC is calculated from comonomer distribution profile by CEF, and CDC is defined as Comonomer Distribution Index divided by Comonomer Distribution Shape Factor multiplying by 100 as shown in Equation 1, Figure 1, and wherein Comonomer distribution index stands for the total weight fraction of polymer chains with the comonomer content ranging from 0.5 of

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median comonomer content (C_{median}) and 1.5 of C_{median} from 35.0 to 119.0°C, and wherein Comonomer Distribution Shape Factor is defined as a ratio of the half width of comonomer distribution profile divided by the standard deviation of comonomer distribution profile from the peak temperature (T_p), and wherein the method comprises the following steps:

- 5 (A) Obtain a weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step increase of 0.200°C from CEF according to Equation 2, as shown in Figure 2;
- (B) Calculate the median temperature (T_{median}) at cumulative weight fraction of 0.500, according to Equation 3, as shown in Figure 3;
- 10 (C) Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve according to Equation 4, as shown in Figure 4;
- (D) Construct a comonomer content calibration curve by using a series of reference materials with known amount of comonomer content, i.e., eleven reference materials with
- 15 narrow comonomer distribution (mono-modal comonomer distribution in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (measured via conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0 mole% are analyzed with CEF at the same experimental conditions specified in CEF experimental sections;
- (E) Calculate comonomer content calibration by using the peak temperature (T_p) of
- 20 each reference material and its comonomer content; The calibration is calculated from each reference material as shown in Formula 4, Figure 4, wherein: R^2 is the correlation constant;
- (F) Calculate Comonomer Distribution Index from the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$, and if T_{median} is higher than 98.0°C, Comonomer Distribution Index is defined as 0.95;
- 25 (G) Obtain Maximum peak height from CEF comonomer distribution profile by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two peaks are identical, then the lower temperature peak is selected); half width is defined as the
- temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched
- 30 forward from 35.0°C, while the rear temperature at the half of the maximum peak is searched backward from 119.0°C, in the case of a well defined bimodal distribution where the difference in the peak temperatures is equal to or greater than the 1.1 times of the sum of half width of each peak, the half width of the inventive ethylene-based polymer composition is calculated as the arithmetic average of the half width of each peak;

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(H) Calculate the standard deviation of temperature (*Stdev*) according Equation 5, as shown in Figure 5.

In some processes, processing aids, such as plasticizers, can also be included in the inventive ethylene-based polymer compositions. These aids include, but are not limited to, the phthalates, such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining, and liquid resins from rosin or petroleum feedstocks. Exemplary classes of oils useful as processing aids include white mineral oil such as KAYDOL oil (Chemtura Corp.; Middlebury, Conn.) and SHELLFLEX 371 naphthenic oil (Shell Lubricants; Houston, Tex.). Another suitable oil is TUFFLO oil (Lyondell Lubricants; Houston, Tex).

In some processes, inventive ethylene-based polymer compositions are treated with one or more stabilizers, for example, antioxidants, such as IRGANOX 1010 and IRGAFOS 168 (Ciba Specialty Chemicals; Glatfbrugg, Switzerland). In general, polymers are treated with one or more stabilizers before an extrusion or other melt processes. In other embodiment processes, other polymeric additives include, but are not limited to, ultraviolet light absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents and anti-blocking agents. The inventive ethylene-based polymer composition may, for example, comprise less than 10 percent by the combined weight of one or more additives, based on the weight of the inventive ethylene-based polymer composition and such additives. A particular benefit of the claimed polymers is the absence of catalyst kill agents, other than water, thus eliminating the need for calcium stearate.

The inventive ethylene-based polymer compositions produced may further be compounded. In some embodiments, one or more antioxidants may further be compounded into the inventive ethylene-based polymer compositions and the compounded inventive ethylene-based polymer compositions is then pelletized. The compounded ethylene-based polymer composition may contain any amount of one or more antioxidants. For example, the compounded inventive ethylene-based polymer compositions may comprise from about 200 to about 600 parts of one or more phenolic antioxidants per one million parts of the inventive ethylene-based polymer compositions. In addition, the compounded ethylene-based polymer composition may comprise from about 800 to about 1200 parts of a phosphite-based antioxidant per one million parts of inventive ethylene-based polymer compositions. The compounded inventive ethylene-based polymer compositions may further comprise from

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about 300 to about 1250 parts of calcium stearate per one million parts of inventive ethylene-based polymer compositions.

Uses

The inventive ethylene-based polymer compositions may be employed in a variety of conventional thermoplastic fabrication processes to produce useful articles, including objects comprising at least one film layer, such as a monolayer film, or at least one layer in a multilayer film prepared by cast, blown, calendered, or extrusion coating processes; molded articles, such as blow molded, injection molded, or rotomolded articles; extrusions; fibers; and woven or non-woven fabrics. Thermoplastic compositions comprising the inventive ethylene-based polymer compositions include blends with other natural or synthetic materials, polymers, additives, reinforcing agents, ignition resistant additives, antioxidants, stabilizers, colorants, extenders, crosslinkers, blowing agents, and plasticizers.

The inventive ethylene-based polymer compositions may be used in producing fibers for other applications. Fibers that may be prepared from the inventive ethylene-based polymer compositions or blends thereof include staple fibers, tow, multicomponent, sheath/core, twisted, and monofilament. Suitable fiber forming processes include spunbonded and melt blown techniques, as disclosed in U.S. Patent Nos. 4,340,563 (Appel, et al.), 4,663,220 (Wisneski, et al.), 4,668,566 (Nohr, et al.), and 4,322,027 (Reba), gel spun fibers as disclosed in U.S. Patent No. 4,413,110 (Kavesh, et al.), woven and nonwoven fabrics, as disclosed in U.S. Patent No. 3,485,706 (May), or structures made from such fibers, including blends with other fibers, such as polyester, nylon or cotton, thermoformed articles, extruded shapes, including profile extrusions and co-extrusions, calendared articles, and drawn, twisted, or crimped yarns or fibers.

Additives and adjuvants may be added to the inventive ethylene-based polymer compositions post-formation. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites, powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or naphthelenic oils; and other natural and synthetic polymers, including other polymers that are or can be made according to the embodiment methods.

Blends and mixtures of the inventive ethylene-based polymer compositions with other polyolefins may be performed. Suitable polymers for blending with the inventive ethylene-based polymer compositions include thermoplastic and non-thermoplastic polymers including

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natural and synthetic polymers. Exemplary polymers for blending include polypropylene, (such as impact modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure, free-radical LDPE, Ziegler-Natta LLDPE, metallocene PE, including multiple
5 reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in U.S. Patent Nos. 6,545,088 (Kolthammer, et al.); 6,538,070 (Cardwell, et al.); 6,566,446 (Parikh, et al.); 5,844,045 (Kolthammer, et al.); 5,869,575 (Kolthammer, et al.); and 6,448,341 (Kolthammer, et al.)), ethylene-vinyl acetate (EVA), ethylene/vinyl alcohol copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block
10 copolymers and hydrogenated derivatives thereof (SBS and SEBS), and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, ethylene and propylene-based copolymers (for example, polymers available under the trade designation VERSIFY™ Plastomers & Elastomers (The Dow Chemical Company), SURPASS™ (Nova Chemicals), and VISTAMAXX™ (ExxonMobil Chemical Co.)) can
15 also be useful as components in blends comprising the inventive ethylene-based polymer compositions.

The inventive ethylene-based polymer compositions may be employed as a sealant resin. Surprisingly, certain Short Chain Branching Distribution (SCBD), as shown by CDC, in combination with certain MWD, and a certain level of long chain branching (LCB) has
20 shown to improve hot tack and heat seal performance, including increased hot-tack and heat-seal strength, lower heat seal and hot tack initiation temperatures, as well as broadening of the hot tack window. The inventive ethylene-based polymer compositions may be employed as a pipe and tubing resin through an optimization of the SCBD and MWD, with low unsaturation levels for improved ESCR (environmental stress crack resistance) and higher
25 PENT (Pennsylvania Edge-Notch Tensile Test). The inventive ethylene-based polymer compositions may be employed in applications where UV stability, weatherability are desired through an optimization of the SCBD and MWD, in combination with low unsaturation levels, as well as low levels of low molecular weight, and high comonomer incorporated oligomers. The inventive ethylene-based polymer compositions may be employed in
30 applications where low levels of plate-out, blooming, die build-up, smoke formation, extractables, taste, and odor are desired through an optimization of the SCBD and MWD with low levels of low molecular weight as well as high comonomer incorporated oligomers. The inventive ethylene-based polymer compositions may be employed in stretch film applications. Surprisingly, certain SCBD, in combination with certain MWD, and a certain

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level of long chain branching (LCB) shows improved stretchability and dynamic puncture resistance.

Definitions

5 The term "composition," as used herein, refers to a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

10 The terms "blend" or "polymer blend," as used herein, refers to an intimate physical mixture (that is, without reaction) of two or more polymers. A blend may or may not be miscible (not phase separated at molecular level). A blend may or may not be phase separated. A blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art. The blend may be effected by physically mixing the two or more polymers on the macro level (for example, melt blending resins or compounding) or the micro level (for example, simultaneous forming within the same reactor).

15 The term "linear," as used herein, refers to polymers where the polymer backbone lacks measurable or demonstrable long chain branches, for example, the polymer is substituted with an average of less than 0.01 long branch per 1000 carbons.

20 The term "polymer," as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term "homopolymer," usually employed to refer to polymers prepared from only one type of monomer, and the term "interpolymer" as defined, below. The terms "ethylene/ α -olefin polymer" is indicative of interpolymers as described.

25 The term "interpolymer," as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers.

The term "ethylene-based polymer" refers to a polymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers) and, optionally, may contain at least one comonomer.

30 The term "ethylene/ α -olefin interpolymer" refers to an interpolymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers) and at least one α -olefin.

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Resin Production

All raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent commercially available under the tradename Isopar E from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to a pressure that is above the reaction pressure, approximate to 750 psig. The solvent and comonomer (1-octene) feed is pressurized via mechanical positive displacement pump to a pressure that is above the reaction pressure, approximately 750 psig.

5 The individual catalyst components are manually batch diluted to specified component concentrations with purified solvent (Isopar E) and pressurized to a pressure that is above the reaction pressure, approximately 750 psig. All reaction feed flows are measured with mass flow meters, independently controlled with computer automated valve control systems.

The continuous solution polymerization reactor system according to the present invention consist of two liquid full, non-adiabatic, isothermal, circulating, and independently controlled loops operating in a series configuration. Each reactor has independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to each reactor is independently temperature controlled to anywhere between 5°C to 50°C and typically 40°C by passing the feed stream through a heat exchanger. The fresh comonomer feed to the polymerization reactors can be manually aligned to add comonomer to one of three choices: the first reactor, the second reactor, or the common solvent and then split between both reactors proportionate to the solvent feed split. The total fresh feed to each polymerization reactor is injected into the reactor at two locations per reactor roughly with equal reactor volumes between each injection location. The fresh feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through specially designed injection stingers and are each separately injected into the same relative location in the reactor with no contact time prior to the reactor. The primary catalyst component feed is computer controlled to maintain the reactor monomer concentration at a specified target. The two cocatalyst components are fed based on calculated specified molar ratios to the primary catalyst component. Immediately following each fresh injection location (either feed or catalyst), the feed streams are mixed with the circulating polymerization reactor contents with Kenics static mixing elements. The contents of each reactor are continuously circulated through heat exchangers responsible for removing

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much of the heat of reaction and with the temperature of the coolant side responsible for maintaining isothermal reaction environment at the specified temperature. Circulation around each reactor loop is provided by a screw pump. The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits the first reactor loop and passes through a control valve (responsible for maintaining the pressure of the first reactor at a specified target) and is injected into the second polymerization reactor of similar design. As the stream exits the reactor, it is contacted with water to stop the reaction. In addition, various additives such as anti-oxidants, can be added at this point. The stream then goes through another set of Kenics static mixing elements to evenly disperse the catalyst kill and additives.

Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passes through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then enters a two stage separation and devolatilization system where the polymer is removed from the solvent, hydrogen, and unreacted monomer and comonomer. The recycled stream is purified before entering the reactor again. The separated and devolatilized polymer melt is pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a hopper. The polymer properties are then validated.

The non-polymer portions removed in the devolatilization step pass through various pieces of equipment, which separate most of the ethylene that is removed from the system to a vent destruction unit (it is, however, recycled in manufacturing units). Most of the solvent is recycled back to the reactor after passing through purification beds. This solvent can still have unreacted co-monomer in it that is fortified with fresh co-monomer prior to re-entry to the reactor. This fortification of the co-monomer is an essential part of the product density control method. This recycle solvent can still have some hydrogen which is then fortified with fresh hydrogen to achieve the polymer molecular weight target. A very small amount of solvent leaves the system as a co-product due to solvent carrier in the catalyst streams and a small amount of solvent that is part of commercial grade co-monomers.

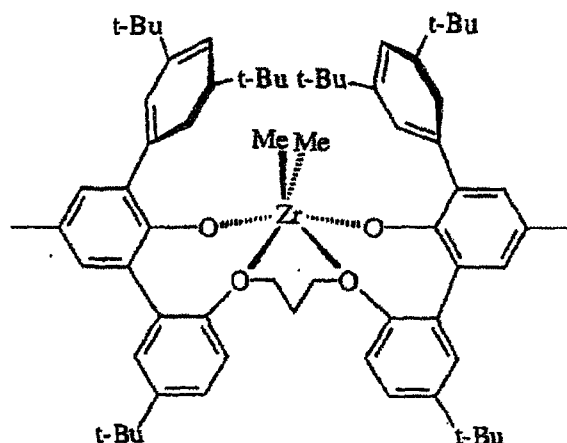
30

Inventive Ethylene-Based Polymer Compositions (Inventive Examples 1-3):

Inventive ethylene-based polymer compositions, i.e. Inventive Example 1-3, are prepared according to the above procedure. The process conditions are reported in Table 1 and Table 2. Inventive Examples 1-3 were tested for various properties according to the test

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methods described below, and these properties are reported in Tables 3-8. Referring to Table 2, MMAO is modified methyl aluminoxane; RIBS-2 is bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) amine; and Zirconium based catalyst is [2,2"-[1,3-propanediylbis(oxy- κ O)]bis[3",5,5"-tris(1,1-dimethylethyl)-5'-methyl[1,1':3,1"-terphenyl]-2'-olato- κ O]]dimethyl-, (OC-6-33)-Zirconium, represented by the following formula:



Comparative Ethylene-Based Compositions (Comparative Examples 1-3):

Comparative Example 1 is 50/50 blend of an ethylene/hexane copolymer having an I_2 of 1 g/10 minutes and density of 0.918 g/cm³, which was provided by The Dow Chemical Company under the tradename EXCEED™ 1018, and an ethylene/hexane copolymer having an I_2 of 3.5 g/10 minutes and density of 0.912 g/cm³, which was also provided by The Dow Chemical Company under the tradename EXCEED™ 3512.

Comparative Example 2 is an ethylene/octane copolymer having I_2 of 1 g/10 minutes and density of 0.916 g/cm³, which was provided by The Dow Chemical Company under the tradename ELITE™ 5400G.

Comparative Example 3 is an ethylene/octane copolymer having I_2 of 1.5 g/10 minutes and density of 0.914 g/cm³, which was provided by The Dow Chemical Company under the tradename ELITE™ 5500.

The Comparative Examples 1-3 were tested for various properties according to the test methods described below, and these properties are reported in Tables 3-8.

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Inventive Films 1 and 3

Inventive ethylene-based polymer compositions, Inventive Example 1 and 3, are blown into Inventive Monolayer Films 1 and 3 on a three layer blown film line. The blown film line consists of three groove fed extruders with single flight screws (25:30:25mm). The length/diameter (L/D) ratio for all screws is 25:1. The blown film line has a 60 mm die with dual lip air ring cooling system, with a screen pack configuration of 20:40:60:80:20 mesh. Inventive Films 1 and 3 are produced at 1 mil thickness. The film fabrication conditions are reported in Table 9. The Inventive Films 1 and 3 are tested for their various properties according to the test methods described below, and these properties are reported in Table 10.

Comparative Films 2 and 3

Comparative ethylene-based polymer compositions, Comparative Example 2 and 3 are blown into Comparative Monolayer Films 2 and 3 on a three layer blown film line. The blown film line consists of three groove fed extruders with single flight screws (25:30:25mm). The length/diameter (L/D) ratio for all screws is 25:1. The blown film line has a 60 mm die with dual lip air ring cooling system, with a screen pack configuration of 20:40:60:80:20 mesh. Comparative Films 2 and 3 are produced at 1 mil thickness. The film fabrication conditions are reported in Table 9. The Comparative Films 2 and 3 are tested for their various properties according to the test methods described below, and these properties are reported in Table 10.

Inventive Three Layer Films A and B

Referring to Tables 11A and B, Inventive Three Layer Films A and B are fabricated according to the following procedure. The Fabrication conditions are reported in Tables 12 and 13.

Inventive Three Layer Film A comprises (1) a sealant layer comprising 96.75 percent by weight of the inventive ethylene-based polymer compositions of Inventive Example 3, 1000 parts per million (ppm) by weight of a slip agent (Erucamide), and 2500 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (2) a core layer comprising 72.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 25 percent by weight of INSPIRE™ 114, a propylene based polymer having a density of approximately 0.900 g/cm³ and a melt flow rate (measured at 230°C and 2.16 kg) of approximately 0.50 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent

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(diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (3) a skin layer comprising 96.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent.

Inventive Three Layer Film B comprises (1) a sealant layer comprising 96.75 percent by weight of the inventive ethylene-based polymer compositions of Inventive Example 1, 1000 parts per million (ppm) by weight of a slip agent (Erucamide), and 2500 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (2) a core layer comprising 72.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 25 percent by weight of INSPIRE™ 114, a propylene based polymer having a density of approximately 0.900 g/cm³ and a melt flow rate (measured at 230°C and 2.16 kg) of approximately 0.50 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (3) a skin layer comprising 96.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent

The inventive three layer co-extruded films are fabricated on a three layer co-extruded blown film line consisting of two 2.5 inch 24:1 L/D Egan extruders (Extruders A and B) and one 2 inch 24:1 L/D Johnson extruder (Extruder C). All the extruders are smooth bore with barrel heating and cooling (closed loop liquid cooling system). The extruders are powered by 60, 75, and 20 HP DC drivers, respectively. The extruders are controlled by an Extrol 6032 microprocessor. The extrusion process is monitored by Pressure Transducers, three on the 2 ½" barrels, one before and one after each breaker plate as well as 4 heater zones on each barrel, one each at the adapter and the block and two zones on the die. The Microprocessor also tracks the extruder RPM, % FLC, HP, Rate, Layflat and melt temperature at each

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extruder. The die is a 6 inch Battenfeld-Gloucester with a layer ratio of 15:75:15% and a 70 mil die gap. The standard screws used are New Castle's single flight high shear screws with a 2.88 compression ratio on Extruder A; Feed Screw's Modified Double mix with a 3.64 compression ratio on Extruder B; and Johnson single flight with a 2.5 compression ratio on Extruder C. Co-extruded film structure of 2.5 mil film (1.0 mil sealant / 1.0 mil core / 0.5 mil skin layer), slit to 21.5", cut flush with core, was produced at a 2.5:1 BUR. The screen pack configuration was 20:40:60:80:20 mesh.

Inventive Three Layer Films A and B are evaluated on a Weigh Pack Systems XPDIUS ELITE series VFS bagger, and the results are shown in Table 14. The Weigh Pack VFFS packaging equipment used poly sealing jaws: false jaws + seal jaws, where the seal jaws back is concave and the front is jaw is convex. The catch plates are V-shaped just above seal jaws. The jaw strength is set at 180 units, based on the servo motor. The fin seal jaw is set at 50 psi dwell pressure.

Bags are tested using 2 lbs of measured dry red beans as the fill product. Pre-measured 2 lbs amounts of dry red beans are poured by hand into the VFFS bags via the forming collar. Products are evaluated for minimum seal temperature and minimum dwell time, two critical parameters for maximization of VFFS production rate. The minimum seal temperature is determined by filling the VFFS bags with 2 lbs worth of dried beans at a constant dwell time (1.35 s) and lowering the seal temperature until the VFFS bags would no longer hold the dried beans. To determine the minimum dwell time pillow pouches are made (VFFS bags with no product). The tests are started at 5°C above the minimum seal temperature required to hold 2 lbs of dried beans. The seal bar dwell time is then shortened until the VFFS bag would no longer hold a seal.

For the minimum seal temperature determination, after the packages are made, they are allowed to "setup" for approximately 30 seconds and then vigorously shook to make sure the content held for the 2 lb bean packages. For the minimum dwell temperature determination the air-filled-only pillow pouches are allowed to setup for approximately 30 second to allow the seal to set-up and then hand pressure is applied to the packages to make sure they would not burst open at the seal or have a large "channel" leaker. A channel leaker is a large hole formed at the point where either of the seals on the ends of the package overlapped with long seal on the long-edge of the package. A hermetic (air-tight) seal is not required for most solid food applications, including frozen foods. The results are reported in Table 14.

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Comparative Three Layer Film A

Referring to Table 11C, Comparative Three Layer Film A is fabricated according to the following procedure. The Fabrication conditions are reported in Tables 12 and 13.

Comparative Three Layer Film A comprises (1) a sealant layer comprising 96.75 percent by weight of ELITE™ 5500G, an ethylene/octane copolymer having a melt index (I₂) (measured at 190°C and 2.16 kg) of approximately 1.5 g/10 minutes and a density of approximately 0.914 g/cm³, 1000 parts per million (ppm) by weight of a slip agent (Erucamide), and 2500 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (2) a core layer comprising 72.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 25 percent by weight of INSPIRE™ 114, a propylene based polymer having a density of approximately 0.900 g/cm³ and a melt flow rate (measured at 230°C and 2.16 kg) of approximately 0.50 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent; (3) a skin layer comprising 96.1 percent by weight of DOWLEX™ 2045. 11G, an ethylene copolymer (ethylene-octene copolymer) having a density of approximately 0.922 g/cm³ and a melt index (measured at 190°C and 2.16 kg) of approximately 1.0 g/10 minutes, 1200 parts per million (ppm) by weight of a slip agent (Erucamide), and 3000 ppm by weight of an antiblocking agent (diamatious earth-antiblock) with the remaining weight being LDPE as the carrier for slip agent and antiblock agent.

Comparative Three Layer Film A is fabricated on a three layer co-extruded blown film line consisting of two 2.5 inch 24:1 L/D Egan extruders (Extruders A and B) and one 2 inch 24:1 L/D Johnson extruder (Extruder C). All the extruders are smooth bore with barrel heating and cooling (closed loop liquid cooling system). The extruders are powered by 60, 75, and 20 HP DC drivers, respectively. The extruders are controlled by an Extrol 6032 microprocessor. The extrusion process is monitored by Pressure Transducers, three on the 2 ½" barrels, one before and one after each breaker plate as well as 4 heater zones on each barrel, one each at the adapter and the block and two zones on the die. The Microprocessor also tracks the extruder RPM, % FLC, HP, Rate, Layflat and melt temperature at each extruder. The die is a 6 inch Battenfeld-Gloucester with a layer ratio of 15:75:15% and a 70 mil die gap. The standard screws used are New Castle's single flight high shear screws with

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a 2.88 compression ratio on Extruder A; Feed Screw's Modified Double mix with a 3.64 compression ratio on Extruder B; and Johnson single flight with a 2.5 compression ratio on Extruder C. Co-extruded film structure of 2.5 mil film (1.0 mil sealant / 1.0 mil core / 0.5 mil skin layer), slit to 21.5", cut flush with core, was produced at a 2.5:1 BUR. The screen pack
 5 configuration was 20:40:60:80:20 mesh.

Comparative Three Layer Film A is evaluated on a Weigh Pack Systems XPDIUS ELITE series VFS bagger. The Weigh Pack VFFS packaging equipment used poly sealing jaws: false jaws + seal jaws, where the seal jaws back is concave and the front is jaw is convex. The catch plates are V-shaped just above seal jaws. The jaw strength is set at 180
 10 units, based on the servo motor. The fin seal jaw is set at 50 psi dwell pressure.

Bags are tested using 2 lbs of measured dry red beans as the fill product. Pre-measured 2 lbs amounts of dry red beans are poured by hand into the VFFS bags via the forming collar. Products are evaluated for minimum seal temperature and minimum dwell time, two critical parameters for maximization of VFFS production rate. The minimum seal
 15 temperature is determined by filling the VFFS bags with 2 lbs worth of dried beans at a constant dwell time (1.35 s) and lowering the seal temperature until the VFFS bags would no longer hold the dried beans. To determine the minimum dwell time pillow pouches are made (VFFS bags with no product). The tests are started at 5°C above the minimum seal temperature required to hold 2 lbs of dried beans. The seal bar dwell time is then shortened
 20 until the VFFS bag would no longer hold a seal.

For the minimum seal temperature determination, after the packages are made, they are allowed to "setup" for approximately 30 seconds and then vigorously shook to make sure the content held for the 2 lb bean packages. For the minimum dwell temperature determination the air-filled-only pillow pouches are allowed to setup for approximately 30
 25 second to allow the seal to set-up and then hand pressure is applied to the packages to make sure they would not burst open at the seal or have a large "channel" leaker. A channel leaker is a large hole formed at the point where either of the seals on the ends of the package overlapped with long seal on the long-edge of the package. A hermetic (air-tight) seal is not required for most solid food applications, including frozen foods. The results are reported in
 30 Table 14.

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Table 1

	Units	Inventive Example 1	Inventive Example 2	Inventive Example 3
Primary Reactor Feed Temperature	°C	20	20	20
Primary Reactor Total Solvent Flow	lbs/hr	1,161	1,160	1159
Primary Reactor Total Ethylene Flow	lbs/hr	178	199	220
Primary Reactor Total Comonomer Flow	lbs/hr	76	15	92
Primary Reactor Feed Solvent/Ethylene Ratio	---	6.9	6.9	5.5
Primary Reactor Fresh Hydrogen Flow	Standard cm ³ /minute	3,383	701	6,485
Secondary Reactor Feed Temperature	°C	21	32	20
Secondary Reactor Total Solvent Flow	lbs/hr	510	340	400
Secondary Reactor Total Ethylene Flow	lbs/hr	196	127	153
Secondary Reactor Total Comonomer Flow	lbs/hr	13.5	1.8	16.1
Secondary Reactor Feed Solvent/Ethylene Ratio	---	2.7	2.8	2.7
Secondary Reactor Fresh Hydrogen Flow	Standard cm ³ /minute	4,990	21,857	2,047
Primary Reactor Control Temperature	°C	140	180	155
Primary Reactor Pressure	psig	725	725	725
Primary Reactor Ethylene Conversion	%	92	91	81
Primary Reactor Percent Solids	%	16	13	16
Secondary Reactor Heat Transfer Coefficient	BTU/hr ft ² °F	6.7	9.1	7.6
Primary Reactor Polymer Residence Time	hrs	0.27	0.29	0.25
Secondary Reactor Control Temperature	°C	190	190	190
Secondary Reactor Pressure	psig	731	730	729
Secondary Reactor Ethylene Conversion	%	87	85	87
Secondary Reactor Percent Solids	%	21	17	22
Secondary Reactor Heat Transfer Coefficient	BTU/hr ft ² °F	51	44	80
Secondary Reactor Polymer Residence Time	hrs	0.10	0.12	0.10
Primary Reactor Split	%	50	56	53
Primary Reactor Production Rate	lbs/hr	212	160	226

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Continuation of Table 1

	Units	Inventive Example 1	Inventive Example 2	Inventive Example 3
Secondary Reactor Production Rate	lbs/hr	215	127	201
Total Production Rate from MB	lbs/hr	426	287	427
Primary Reactor Catalyst Efficiency	10 ⁶ Lbs	8.6	2.3	10.9
Secondary Reactor Catalyst Efficiency	10 ⁶ Lbs	1.6	1.1	1.4

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Table 2

	Units	Inventive Example 1	Inventive Example 2	Inventive Example 3
Primary Reactor Catalyst Flow	lbs/hr	1.81	1.962134	1.52
Primary Reactor Catalyst Concentration	ppm	13.67	34.95987	13.67
Primary Reactor Catalyst Efficiency	10 ⁹ lbs	8.56	2.309096	10.87
Primary Reactor Catalyst- Type 1	---	Zirconium Based Catalyst	Zirconium Based Catalyst	Zirconium Based Catalyst
Primary Reactor Catalyst - 1 Flow	lbs/hr	1.81	1.96	1.52
Primary Reactor Catalyst - 1 Concentration	ppm	13.67	34.96	13.67
Primary Reactor Catalyst - 1	Mole Weight	90.86	90.86	90.86
Primary Reactor Co-Catalyst - 1	Molar Ratio	1.48	1.42	1.77
Primary Reactor Co-Catalyst- 1 Type	---	MMAO	MMAO	MMAO
Primary Reactor Co-Catalyst- 1 Flow	lbs/hr	0.81	1.19	0.81
Primary Reactor Co-Catalyst- 1 Concentration	ppm	598	1,094	596
Primary Reactor Co-Catalyst - 2	Molar Ratio	6.91	6.97	7.11
Primary Reactor Co-Catalyst- 2 Type	---	RIBS-2	RIBS-2	RIBS-2
Primary Reactor Co-Catalyst- 2 Flow	lbs/hr	0.52	0.72	0.44
Primary Reactor Co-Catalyst- 2 Concentration	ppm	99.6	199	99.6
Secondary Reactor Catalyst Type	---	Zirconium Based Catalyst	Zirconium Based Catalyst	Zirconium Based Catalyst
Secondary Reactor Catalyst Flow	lbs/hr	2.30	1.54	3.52
Secondary Reactor Catalyst Concentration	ppm	60	76	40
Secondary Reactor Catalyst Efficiency	10 ⁶ lbs	1.56	1.08	1.43
Secondary Reactor Co-Catalyst - 1	Molar Ratio	1.50	1.21	
Secondary Reactor Co-Catalyst- 1 Type	---	MMAO	MMAO	MMAO
Secondary Reactor Co-Catalyst- 1 Flow	lbs/hr	4.59	1.68	4.62

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Continuation of Table 2

	Units	Inventive Example 1	Inventive Example 2	Inventive Example 3
Secondary Reactor Co-Catalyst - 2	Molar Ratio	7.02	6.96	6.99
Secondary Reactor Co-Catalyst- 2 Type	---	RIBS-2	RIBS-2	RIBS-2
Secondary Reactor Co-Catalyst- 2 Flow	lbs/hr	2.88	1.22	2.93
Secondary Reactor Co-Catalyst- 2 Concentration	ppm	100	199	100

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Table 3

	Density(g/cc)	I ₁₀ (g/10 min)	I ₂ (g/10 min)	I ₁₀ /I ₂
Inventive Example 1	0.912	11.5	1.5	7.7
Inventive Example 2	0.937	7.1	0.4	16.1
Inventive Example 3	0.912	11.5	1.6	7.4
Comparative Example 1	0.916	9.1	1.6	5.9
Comparative Example 2	0.916	8.5	1.0	8.4
Comparative Example 3	0.914	11.2	1.5	7.3

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Table 4

	Unsaturation Unit/1,000,000 C				
	vinylene	trisubstituted	vinyl	vinylidene	Total
Inventive Example 1	6	2	47	7	62
Inventive Example 2	5	1	59	6	71
Inventive Example 3	9	2	55	12	78
Comparative Example 1	21	46	54	24	145
Comparative Example 2	52	51	171	40	314
Comparative Example 3	41	32	149	30	252

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Table 5

	Comonomer Distribution Index	Stdev, C	Half Width	Half Width/ Stdev	CDC (Comonomer Distribution Constant)
Inventive Example 1	0.873	12.301	16.823	1.368	63.8
Inventive Example 2	0.838	6.250	3.721	0.595	140.9
Inventive Example 3	0.802	11.003	5.788	0.526	152.4
Comparative Example 1	0.662	10.508	25.270	2.405	27.5
Comparative Example 2	0.515	18.448	36.739	1.991	25.9
Comparative Example 3	0.246	27.884	42.670	1.530	16.1

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Table 6

	Cool Curve Data		Heat Curve Data	
	T _c (°C)	ΔH of Crystallization (J/g)	T _m (°C)	ΔH of melting (J/g)
Inventive Example 1	95.21	130.7	110.82	132.2
Inventive Example 2	112.97	179.6	123.79	178.4
Inventive Example 3	93.97	130.4	108.33	131.7
Comparative Example 1	103.92	126.7	117.55	129.5
Comparative Example 2	105.1	141.6	123.63	143
Comparative Example 3	106.55	137.5	124	137.4

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Table 7

Identification	Test Method	Mn	Mw	Mz	Mw/Mn
Inventive Example 1	Conventional GPC	32,370	86,200	170,500	2.7
Inventive Example 2	Conventional GPC	14,630	103,100	282,600	7.0
Inventive Example 3	Conventional GPC	33,750	84,080	159,600	2.5
Comparative Example 1	Conventional GPC	36,780	95,950	174,500	2.6
Comparative Example 2	Conventional GPC	24,600	101,900	238,200	4.1
Comparative Example 3	Conventional GPC	28,800	105,100	374,900	3.6

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Table 8

Shear Rate (1/sec) @ 190°C	G' (Pa)				G'' (Pa)				Eta* (Pa-s)			
	0.1	1	10	100	0.1	1	10	100	0.1	1	10	100
Inventive Example 1	66	1,221	12,621	85,376	620	4,696	27,476	102,830	6,240	4,825	3,024	1,337
Inventive Example 2	1,764	7,855	30,375	111,000	2,756	9,716	33,986	87,314	32,724	12,494	4,558	1,412
Inventive Example 3	52	1,054	11,539	84,139	569	4,411	26,910	103,850	5,716	4,535	2,928	1,337
Comparative Example 1	8	270	8,214	97,443	378	3,670	29,450	128,860	3,781	3,679	3,057	1,616
Comparative Example 2	199	2,134	18,203	102,500	957	6,275	32,869	104,710	9,775	6,628	3,757	1,465
Comparative Example 3	34	892	11,631	86,949	529	4,404	27,610	104,400	5,296	4,493	2,996	1,359

Table 9

Parameter	Unit	Inventive Film 1		Comparative Film 2		Comparative Film 3		Inventive Film 3	
Actual Speed	m/min	17.3		22.2		17.4		17.3	
Actual Rate	kg/hr	27.6		10.9		13.2		14.7	
Motor Load	Amp	6		6		6		6	
Screw Speed	rpm	50		50		50		50	
Pressure	Bar	289		306		300		287	
Melt Temperature	°C	186		N/A (Instrumentation Failure)		185		185	
Layflat Width	cm	23.8		23.5		23.8		23.8	
Temperature Profile		Set	Actual	Set	Actual	Set	Actual	Set	Actual
Core Barrel 1	°C	180	180	170	170	180	180	180	180
Core Barrel 2	°C	195	196	220	220	195	195	195	194
Core Barrel 3	°C	190	189	175	175	190	189	190	189
Core Barrel 4	°C	190	189	175	175	190	191	190	191
Adapter Temperature	°C	210	210	225	225	210	210	210	210
Tube	°C	210	210	225	225	210	210	210	210
Die Temperature 5	°C	210	210	225	225	210	210	210	210
Die Temperature 4	°C	210	210	225	225	210	210	210	210
Die Temperature 3	°C	210	210	225	225	210	210	210	210
Die Temperature 2	°C	210	210	225	226	210	210	210	210
Die Temperature 1	°C	210	210	225	225	210	210	210	210
Die Gap	mil	2		2		2		2	
Frost Line	inch	7		7		7		7	
BUR		2.5		2.5		2.5		2.5	

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Table 10

	Inventive Film 1	Inventive Film 3	Comparative Film 2	Comparative Film 3
Gloss 45 deg (%)	76	83	78	91
Haze- Film (%)	7	5	6	4
Haze Internal (%)	0.6	0.5	1.3	1.3
Dart A (g)	850	850	850	703
Dart B (g)	580	676	666	-
Elmendorf Tear MD Normalized (g/mil)	334	378	256	376
Elmendorf Tear CD Normalized (g/mil)	465	521	535	614
Puncture (ft*lb/in(3'))	237	342	399	146
Tensile- CD- Break Stress (psi)	6,336	6,811	7,039	6,419
Tensile- CD- Energy to Break (in*lb)	32	34	33	34
Tensile- CD- Strain to Break (%)	641	670	678	666
Tensile- CD- Stress at Yield (psi)	1,419	1,404	1,595	1,477
Tensile- MD- Break Stress (psi)	6,830	7,417	7,320	7,046
Tensile- MD- Energy to Break (in*lb)	26	28	24	30
Tensile- MD- Strain to Break (%)	476	506	436	525
Tensile- MD- Stress at Yield (psi)	1,713	1,684	1,607	1,654

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Table 11A
Inventive Three Layer Film A

For Sealant Layer	Inventive Example 3 + Slip Agent + Antiblock Agent	96.75 wt% Inventive Example 3	2.0 wt% Slip Agent (LDPE based)	1.25 wt% Antiblock Agent (LDPE based)	1000 ppm Slip Agent in Sealant Layer	2500 ppm Antiblock in Sealant Layer
For Skin Layer	DOWLEX 2045.11G + Slip Agent + Antiblock Agent	96.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Skin Layer	3000 ppm Antiblock in Skin Layer
For Core Layer	DOWLEX 2045.11G + 25 wt% INSPIRE 114 PP + Slip Agent + Antiblock Agent	72.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Core Layer	3000 ppm Antiblock in Core Layer

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Table 11B
Inventive Three Layer Film B

For Sealant Layer	Inventive Example 1 + Slip Agent + Antiblock Agent	96.75 wt% Inventive Example 1	2.0 wt% Slip Agent (LDPE based)	1.25 wt% Antiblock Agent (LDPE based)	1000 ppm Slip Agent in Sealant Layer	2500 ppm Antiblock in Sealant Layer
For Skin Layer	DOWLEX 2045.11G + Slip Agent + Antiblock Agent	96.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Skin Layer	3000 ppm Antiblock in Skin Layer
For Core Layer	DOWLEX 2045.11G + 25 wt% INSPIRE 114 PP + Slip Agent + Antiblock Agent	72.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Core Layer	3000 ppm Antiblock in Core Layer

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Table 11C
Comparative Three Layer Film A

For Sealant Layer	Comparative Example 3 + Slip Agent + Antiblock Agent	96.75 wt% ELITE 5500G	2.0 wt% Slip Agent (LDPE based)	1.25 wt% Antiblock (LDPE based)	1000 ppm Slip Agent in Sealant Layer	2500 ppm Antiblock in Sealant Layer
For Skin Layer	DOWLEX 2045.11G + Slip Agent + Antiblock Agent	96.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Skin Layer	3000 ppm Antiblock in Skin Layer
For Core Layer	DOWLEX 2045.11G + 25 wt% INSPIRE 114 PP + Slip Agent + Antiblock Agent	72.1 wt% DOWLEX 2045.11G	2.4 wt% Slip Agent (LDPE based)	1.5 wt% Antiblock Agent (LDPE based)	1200 ppm Slip Agent in Core Layer	3000 ppm Antiblock in Core Layer

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Table 12

		Inventive Three Layer Film A					
		Sealant Layer		Core Layer		Skin Layer	
Parameter	Unit						
Actual Speed	RPM	47.2		48.1		29.5	
Actual Rate	lb/hr	63.6		64		32.4	
Layer Ratio	%	40		40		20	
% FLC		56.9		37.1		15.3	
HP		13		7		2	
Pressure 1	psi	-		1,060		-	
Pressure 2	psi	2,050		1,230		-	
Pressure 3	psi	5,780		2,700		-	
Screen Pressure	psi	5,310		-		4,200	
Adaptor Pressure	psi	4,170		2,480		3,500	
Melt Temperature	°F	422		425		414	
Layflat Width	cm	60		60		60	
		Layer A		Layer B		Layer C	
Temperature Profile		Set	Actual	Set	Actual	Set	Actual
Barrel 1	°F	375	375	375	375	375	377
Barrel 2	°F	425	425	425	425	425	426
Barrel 3	°F	380	380	380	383	400	400
Barrel 4	°F	380	377	380	381	400	400
Adapter	°F	400	400	400	400	420	420
Block	°F			450	446		
Lower Die	°F			450	450		
Upper Die	°F			450	450		
Inner Die				450	450		
External Air Temp	°C			45	45		
Internal Air Temp	°C			45	75		
Die Gap	mil			70			
Overall Speed	RPM			53.6			
Overall Rate	lb/hr			160			
BUR				2.5			

Table 13

Parameter	Unit	Inventive Three Layer Film B						Comparative Three Layer Film A					
		Sealant Layer		Core Layer		Skin Layer		Sealant Layer		Core Layer		Skin Layer	
Actual Speed	RPM	48.2		47.6		29.1		50.1		48.5		29.5	
Actual Rate	lb/hr	64.4		64.3		32.1		63.5		64.3		32.5	
Layer Ratio	%	40		40		20		40		40		20	
% FLC		57.7		36.5		15.2		58.2		37.3		15.6	
HP		13		7		2		14		7		2	
Pressure 1	psi	-		1,130		-		-		1,080		-	
Pressure 2	psi	2,570		1,490		-		1,950		1,120		-	
Pressure 3	psi	5,500		2,720		-		5,750		2,750		-	
Screen Pressure	psi	5,460		-		4,120		5,460		-		4,260	
Adaptor Pressure	psi	4,260		2,470		3,450		4,380		2,530		3,540	
Melt Temperature	°F	426		424		415		425		425		413	
Layflat Width	cm	60		60		60		60		60		60	
		Layer A		Layer B		Layer C		Layer A		Layer B		Layer C	
Temperature Profile		Set	Actual	Set	Actual	Set	Actual	Set	Actual	Set	Actual	Set	Actual
Barrel 1	°F	375	376	375	375	375	374	375	376	375	375	375	374
Barrel 2	°F	425	425	425	426	425	425	425	425	425	426	425	425
Barrel 3	°F	380	382	380	376	400	400	380	380	380	381	400	400
Barrel 4	°F	380	385	380	383	400	400	380	385	380	381	400	400
Adapter	°F	400	400	400	399	420	420	400	400	400	400	420	421
Block	°F			450	448					450	447		
Lower Die	°F			450	450					450	450		
Upper Die	°F			450	450					450	450		
Inner Die				450	450					450	451		
External Air Temp	°C			45	45					45	45		

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Continuation of Table 13

		Inventive Three Layer Film B			Comparative Three Layer Film A		
		Sealant Layer	Core Layer	Sealant Layer	Core Layer	Sealant Layer	Core Layer
Parameter	Unit						
Temperature Profile							
Die Gap	mil		70			70	
Overall Speed	RPM		50.8			53.6	
Overall Rate	lb/hr		161			160	
BUR			2.5			2.5	

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Table 14

Film	Minimum Seal Temperature 2 lb fill weight / 1.35 seconds dwell time		Minimum dwell time Air fill / Minimum fill temperature	
	HTIT (°C)	Dwell Time (s)	HTIT (°C)	Dwell Time (s)
Comparative Three Layer Film A	Fail	Fail	140	2
Inventive Three Layer Film A	130	1.35	135	1.15
Inventive Three Layer Film B	135	1.35	135	1.25

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TEST METHODS**Density**

Samples that are measured for density are prepared according to ASTM D-
5 1928. Measurements are made within one hour of sample pressing using ASTM D-
792, Method B.

Melt Index

Melt index, or I_2 , is measured in accordance with ASTM-D 1238, Condition
190 °C/2.16 kg, and is reported in grams eluted per 10 minutes. I_{10} is measured in
10 accordance with ASTM-D 1238, Condition 190 °C/10 kg, and is reported in grams
eluted per 10 minutes.

DSC Crystallinity

Differential Scanning Calorimetry (DSC) can be used to measure the melting
and crystallization behavior of a polymer over a wide range of temperature. For
15 example, the TA Instruments Q1000 DSC, equipped with an RCS (refrigerated
cooling system) and an autosampler is used to perform this analysis. During testing, a
nitrogen purge gas flow of 50 ml/min is used. Each sample is melt pressed into a thin
film at about 175 °C; the melted sample is then air-cooled to room temperature (~25
°C). A 3-10 mg, 6 mm diameter specimen is extracted from the cooled polymer,
20 weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis is
then performed to determine its thermal properties.

The thermal behavior of the sample is determined by ramping the sample
temperature up and down to create a heat flow versus temperature profile. First, the
sample is rapidly heated to 180 °C and held isothermal for 3 minutes in order to
25 remove its thermal history. Next, the sample is cooled to -40 °C at a 10 °C/minute
cooling rate and held isothermal at -40 °C for 3 minutes. The sample is then heated to
150 °C (this is the "second heat" ramp) at a 10 °C/minute heating rate. The cooling
and second heating curves are recorded. The cool curve is analyzed by setting
baseline endpoints from the beginning of crystallization to -20 °C. The heat curve is
30 analyzed by setting baseline endpoints from -20 °C to the end of melt. The values
determined are peak melting temperature (T_m), peak crystallization temperature (T_c),
heat of fusion (H_f) (in Joules per gram), and the calculated % crystallinity for
polyethylene samples using Equation 6, shown in Figure 6.

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The heat of fusion (H_f) and the peak melting temperature are reported from the second heat curve. Peak crystallization temperature is determined from the cooling curve.

Dynamic Mechanical Spectroscopy (DMS) Frequency Sweep

- 5 Melt rheology, constant temperature frequency sweeps, were performed using a TA Instruments Advanced Rheometric Expansion System (ARES) rheometer equipped with 25 mm parallel plates under a nitrogen purge. Frequency sweeps were performed at 190 °C for all samples at a gap of 2.0 mm and at a constant strain of 10%. The frequency interval was from 0.1 to 100 radians/second. The stress response
10 was analyzed in terms of amplitude and phase, from which the storage modulus (G'), loss modulus (G''), and dynamic melt viscosity (η^*) were calculated.

Gel Permeation Chromatography (GPC)

- The GPC system consists of a Waters (Milford, MA) 150°C high temperature chromatograph (other suitable high temperatures GPC instruments include Polymer
15 Laboratories (Shropshire, UK) Model 210 and Model 220) equipped with an on-board differential refractometer (RI). Additional detectors can include an IR4 infra-red detector from Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, MA) 2-angle laser light scattering detector Model 2040, and a Viscotek (Houston, TX) 150R 4-capillary solution viscometer. A GPC with the last two independent detectors
20 and at least one of the first detectors is sometimes referred to as "3D-GPC", while the term "GPC" alone generally refers to conventional GPC. Depending on the sample, either the 15-degree angle or the 90-degree angle of the light scattering detector is used for calculation purposes. Data collection is performed using Viscotek TriSEC software, Version 3, and a 4-channel Viscotek Data Manager DM400. The system is
25 also equipped with an on-line solvent degassing device from Polymer Laboratories (Shropshire, UK). Suitable high temperature GPC columns can be used such as four 30 cm long Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron mixed-pore-size packing (MixA LS, Polymer Labs). The sample carousel compartment is operated at 140 °C and the column compartment is operated
30 at 150 °C. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contain 200 ppm of butylated hydroxytoluene (BHT). Both solvents are sparged with nitrogen. The polyethylene samples are gently stirred at 160 °C for four

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hours. The injection volume is 200 microliters. The flow rate through the GPC is set at 1 ml/minute.

The GPC column set is calibrated before running the Examples by running twenty-one narrow molecular weight distribution polystyrene standards. The molecular weight (MW) of the standards ranges from 580 to 8,400,000 grams per mole, and the standards are contained in 6 "cocktail" mixtures. Each standard mixture has at least a decade of separation between individual molecular weights. The standard mixtures are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular weights equal to or greater than 1,000,000 grams per mole and 0.05 g in 50 ml of solvent for molecular weights less than 1,000,000 grams per mole. The polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene M_w using the Mark-Houwink K and a (sometimes referred to as α) values mentioned later for polystyrene and polyethylene. See the Examples section for a demonstration of this procedure.

With 3D-GPC, absolute weight average molecular weight (" $M_{w, Abs}$ ") and intrinsic viscosity are also obtained independently from suitable narrow polyethylene standards using the same conditions mentioned previously. These narrow linear polyethylene standards may be obtained from Polymer Laboratories (Shropshire, UK; Part No.'s PL2650-0101 and PL2650-0102).

The systematic approach for the determination of multi-detector offsets is performed in a manner consistent with that published by Balke, Mourey, et al. (Mourey and Balke, *Chromatography Polym.*, Chapter 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.*, Chapter 13, (1992)), optimizing triple detector log (M_w and intrinsic viscosity) results from Dow 1683 broad polystyrene (American Polymer Standards Corp.; Mentor, OH) or its equivalent to the narrow standard column calibration results from the narrow polystyrene standards calibration curve. The molecular weight data, accounting for detector volume off-set determination, are obtained in a manner consistent with that published by Zimm (Zimm, B.H., *J. Chem. Phys.*, 16, 1099 (1948)) and Kratochvil (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used in the determination of the molecular weight

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is obtained from the mass detector area and the mass detector constant derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards. The calculated molecular weights are obtained using a light scattering constant derived from one or more of the polyethylene standards mentioned and a refractive index concentration coefficient, dn/dc , of 0.104. Generally, the mass detector response and the light scattering constant should be determined from a linear standard with a molecular weight in excess of about 50,000 daltons. The viscometer calibration can be accomplished using the methods described by the manufacturer or alternatively by using the published values of suitable linear standards such as Standard Reference Materials (SRM) 1475a, 1482a, 1483, or 1484a. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd virial coefficient effects (concentration effects on molecular weight).

g' by 3D-GPC

The index (g') for the sample polymer is determined by first calibrating the light scattering, viscosity, and concentration detectors described in the Gel Permeation Chromatography method *supra* with SRM 1475a homopolymer polyethylene (or an equivalent reference). The light scattering and viscometer detector offsets are determined relative to the concentration detector as described in the calibration. Baselines are subtracted from the light scattering, viscometer, and concentration chromatograms and integration windows are then set making certain to integrate all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the refractive index chromatogram. A linear homopolymer polyethylene is used to establish a Mark-Houwink (MH) linear reference line by injecting a broad molecular weight polyethylene reference such as SRM1475a standard, calculating the data file, and recording the intrinsic viscosity (IV) and molecular weight (M_w), each derived from the light scattering and viscosity detectors respectively and the concentration as determined from the RI detector mass constant for each chromatographic slice. For the analysis of samples the procedure for each chromatographic slice is repeated to obtain a sample Mark-Houwink line. Note that for some samples the lower molecular weights, the intrinsic viscosity and the molecular weight data may need to be extrapolated such that the measured molecular weight and intrinsic viscosity asymptotically approach a linear homopolymer GPC calibration curve. To this end, many highly-branched ethylene-based polymer samples require that the linear

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reference line be shifted slightly to account for the contribution of short chain branching before proceeding with the long chain branching index (g') calculation.

A g' -prime (g'_i) is calculated for each branched sample chromatographic slice (i) and measuring molecular weight (M_i) according to Equation 7, as shown in Figure 5 7, where the calculation utilizes the $IV_{\text{linear reference},j}$ at equivalent molecular weight, M_j , in the linear reference sample. In other words, the sample IV slice (i) and reference IV slice (j) have the same molecular weight ($M_i = M_j$). For simplicity, the $IV_{\text{linear reference},j}$ slices are calculated from a fifth-order polynomial fit of the reference Mark-Houwink Plot. The IV ratio, or g'_i , is only obtained at molecular weights greater than 10 3,500 because of signal-to-noise limitations in the light scattering data. The number of branches along the sample polymer (B_n) at each data slice (i) can be determined by using Equation 8, as shown in Figure 8, assuming a viscosity shielding epsilon factor of 0.75.

Finally, the average LCBf quantity per 1000 carbons in the polymer across all 15 of the slices (i) can be determined using Equation 9, as shown in Figure 9.

gpcBR Branching Index by 3D-GPC

In the 3D-GPC configuration the polyethylene and polystyrene standards can be used to measure the Mark-Houwink constants, K and α , independently for each of the two polymer types, polystyrene and polyethylene. These can be used to refine the 20 Williams and Ward polyethylene equivalent molecular weights in application of the following methods.

The gpcBR branching index is determined by first calibrating the light scattering, viscosity, and concentration detectors as described previously. Baselines are then subtracted from the light scattering, viscometer, and concentration 25 chromatograms. Integration windows are then set to ensure integration of all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the refractive index chromatogram. Linear polyethylene standards are then used to establish polyethylene and polystyrene Mark-Houwink constants as described previously. 30 Upon obtaining the constants, the two values are used to construct two linear reference conventional calibrations ("cc") for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution volume, as shown in Equations 10 and 11, Figures 10 and 11, respectively.

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The gpcBR branching index is a robust method for the characterization of long chain branching. See Yau, Wallace W., "Examples of Using 3D-GPC – TREF for Polyolefin Characterization", *Macromol. Symp.*, 2007, 257, 29-45. The index avoids the slice-by-slice 3D-GPC calculations traditionally used in the determination of g' values and branching frequency calculations in favor of whole polymer detector areas and area dot products. From 3D-GPC data, one can obtain the sample bulk M_w by the light scattering (LS) detector using the peak area method. The method avoids the slice-by-slice ratio of light scattering detector signal over the concentration detector signal as required in the g' determination.

The area calculation in Equation 12, shown in Figure 12, offers more precision because as an overall sample area it is much less sensitive to variation caused by detector noise and GPC settings on baseline and integration limits. More importantly, the peak area calculation is not affected by the detector volume offsets. Similarly, the high-precision sample intrinsic viscosity (IV) is obtained by the area method shown in Equation 13, as shown in Figure 13, where DP_i stands for the differential pressure signal monitored directly from the online viscometer.

To determine the gpcBR branching index, the light scattering elution area for the sample polymer is used to determine the molecular weight of the sample. The viscosity detector elution area for the sample polymer is used to determine the intrinsic viscosity (IV or $[\eta]$) of the sample.

Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a or an equivalent, are determined using the conventional calibrations for both molecular weight and intrinsic viscosity as a function of elution volume, per Equations 14 and 15, as shown in Figures 14 and 15, respectively.

Equation 16, as shown in Figure 16, is used to determine the gpcBR branching index, where $[\eta]$ is the measured intrinsic viscosity, $[\eta]_{cc}$ is the intrinsic viscosity from the conventional calibration, M_w is the measured weight average molecular weight, and $M_{w,cc}$ is the weight average molecular weight of the conventional calibration. The M_w by light scattering (LS) using Equation 12, as shown in Figure 12, is commonly referred to as the absolute M_w ; while the $M_{w,cc}$ from Equation 14, as shown in Figure 14, using the conventional GPC molecular weight calibration curve is often referred to as polymer chain M_w . All statistical values with the "cc" subscript are determined using their respective elution volumes, the corresponding conventional

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calibration as previously described, and the concentration (C_i) derived from the mass detector response. The non-subscripted values are measured values based on the mass detector, LALLS, and viscometer areas. The value of K_{PE} is adjusted iteratively until the linear reference sample has a gpcBR measured value of zero. For example, the
5 final values for α and Log K for the determination of gpcBR in this particular case are 0.725 and -3.355, respectively, for polyethylene, and 0.722 and -3.993 for polystyrene, respectively.

Once the K and α values have been determined, the procedure is repeated using the branched samples. The branched samples are analyzed using the final
10 Mark-Houwink constants as the best "cc" calibration values and applying Equations 12-16, as shown in Figure 12-16, respectively.

The interpretation of gpcBR is straight forward. For linear polymers, gpcBR calculated from Equation 16, as shown in Figure 16, will be close to zero since the values measured by LS and viscometry will be close to the conventional calibration
15 standard. For branched polymers, gpcBR will be higher than zero, especially with high levels of LCB, because the measured polymer M_w will be higher than the calculated $M_{w,cc}$, and the calculated IV_{cc} will be higher than the measured polymer Intrinsic Viscosity (IV). In fact, the gpcBR value represents the fractional IV change due the molecular size contraction effect as the result of polymer branching. A
20 gpcBR value of 0.5 or 2.0 would mean a molecular size contraction effect of IV at the level of 50% and 200%, respectively, versus a linear polymer molecule of equivalent weight.

For these particular Examples, the advantage of using gpcBR in comparison to the g' index and branching frequency calculations is due to the higher precision of
25 gpcBR. All of the parameters used in the gpcBR index determination are obtained with good precision and are not detrimentally affected by the low 3D-GPC detector response at high molecular weight from the concentration detector. Errors in detector volume alignment also do not affect the precision of the gpcBR index determination. In other particular cases, other methods for determining M_w moments may be
30 preferable to the aforementioned technique.

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CEF Method

Comonomer distribution analysis is performed with Crystallization Elution Fractionation (CEF) (PolymerChar in Spain) (B Monrabal et al, Macromol. Symp. 257, 71-79 (2007)). Ortho-dichlorobenzene (ODCB) with 600ppm antioxidant butylated hydroxytoluene (BHT) is used as solvent. Sample preparation is done with autosampler at 160°C for 2 hours under shaking at 4 mg/ml (unless otherwise specified). The injection volume is 300 µl. The temperature profile of CEF is: crystallization at 3°C/min from 110°C to 30°C, the thermal equilibrium at 30°C for 5 minutes, elution at 3°C/min from 30°C to 140°C. The flow rate during crystallization is at 0.052 ml/min. The flow rate during elution is at 0.50 ml/min. The data is collected at one data point/second.

CEF column is packed by the Dow Chemical Company with glass beads at 125 µm± 6% (MO-SCI Specialty Products) with 1/8 inch stainless tubing. Glass beads are acid washed by MO-SCI Specialty with the request from the Dow Chemical Company. Column volume is 2.06 ml. Column temperature calibration is performed by using a mixture of NIST Standard Reference Material Linear polyethylene 1475a (1.0mg/ml) and Eicosane (2mg/ml) in ODCB. Temperature is calibrated by adjusting elution heating rate so that NIST linear polyethylene 1475a has a peak temperature at 101.0°C, and Eicosane has a peak temperature of 30.0°C. The CEF column resolution is calculated with a mixture of NIST linear polyethylene 1475a (1.0mg/ml) and hexacontane (Fluka, purum, ≥97.0%, 1mg/ml). A baseline separation of hexacontane and NIST polyethylene 1475a is achieved. The area of hexacontane (from 35.0 to 67.0°C) to the area of NIST 1475a from 67.0 to 110.0°C is 50 to 50, the amount of soluble fraction below 35.0°C is <1.8 wt%. The CEF column resolution is defined in equation 17, as shown in Figure 17, where the column resolution is 6.0.

CDC Method

Comonomer distribution constant (CDC) is calculated from comonomer distribution profile by CEF. CDC is defined as Comonomer Distribution Index divided by Comonomer Distribution Shape Factor multiplying by 100 as shown in Equation 1, Figure 1.

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Comonomer distribution index stands for the total weight fraction of polymer chains with the comonomer content ranging from 0.5 of median comonomer content (C_{median}) and 1.5 of C_{median} from 35.0 to 119.0°C. Comonomer Distribution Shape Factor is defined as a ratio of the half width of comonomer distribution profile divided
 5 by the standard deviation of comonomer distribution profile from the peak temperature (T_p).

CDC is calculated from comonomer distribution profile by CEF, and CDC is defined as Comonomer Distribution Index divided by Comonomer Distribution Shape Factor multiplying by 100 as shown in Equation 1, Figure 1, and wherein Comonomer
 10 distribution index stands for the total weight fraction of polymer chains with the comonomer content ranging from 0.5 of median comonomer content (C_{median}) and 1.5 of C_{median} from 35.0 to 119.0°C, and wherein Comonomer Distribution Shape Factor is defined as a ratio of the half width of comonomer distribution profile divided by the standard deviation of comonomer distribution profile from the peak temperature (T_p).

15 CDC is calculated according to the following steps:

(A) Obtain a weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step increase of 0.200°C from CEF according to Equation 2, as shown in Figure 2;

(B) Calculate the median temperature (T_{median}) at cumulative weight fraction of
 20 0.500, according to Equation 3, as shown in Figure 3;

(C) Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve according to Equation 4, as shown in Figure 4;

(D) Construct a comonomer content calibration curve by using a series of
 25 reference materials with known amount of comonomer content, i.e., eleven reference materials with narrow comonomer distribution (mono-modal comonomer distribution in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (measured via conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0 mole% are analyzed with CEF at the same experimental conditions specified in
 30 CEF experimental sections;

(E) Calculate comonomer content calibration by using the peak temperature (T_p) of each reference material and its comonomer content; The calibration is calculated from each reference material as shown in Formula 4, Figure 4, wherein: R^2 is the correlation constant;

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(F) Calculate Comonomer Distribution Index from the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$, and if T_{median} is higher than 98.0°C , Comonomer Distribution Index is defined as 0.95;

(G) Obtain Maximum peak height from CEF comonomer distribution profile
 5 by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two peaks are identical, then the lower temperature peak is selected); half width is defined as the temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched forward from 35.0°C , while the rear temperature at the
 10 half of the maximum peak is searched backward from 119.0°C , in the case of a well defined bimodal distribution where the difference in the peak temperatures is equal to or greater than the 1.1 times of the sum of half width of each peak, the half width of the inventive ethylene-based polymer composition is calculated as the arithmetic average of the half width of each peak;

15 (H) Calculate the standard deviation of temperature (*Stdev*) according Equation 5, as shown in Figure 5.

Creep zero shear viscosity measurement method:

Zero-shear viscosities are obtained via creep tests that were conducted on an AR-G2 stress controlled rheometer (TA Instruments; New Castle, Del) using 25-mm-
 20 diameter parallel plates at 190°C . The rheometer oven is set to test temperature for at least 30 minutes prior to zeroing fixtures. At the testing temperature a compression molded sample disk is inserted between the plates and allowed to come to equilibrium for 5 minutes. The upper plate is then lowered down to $50\text{ }\mu\text{m}$ above the desired testing gap (1.5 mm). Any superfluous material is trimmed off and the upper plate is
 25 lowered to the desired gap. Measurements are done under nitrogen purging at a flow rate of 5 L/min. Default creep time is set for 2 hours.

A constant low shear stress of 20 Pa is applied for all of the samples to ensure that the steady state shear rate is low enough to be in the Newtonian region. The resulting steady state shear rates are in the range of 10^{-3} to 10^{-4} s^{-1} for the samples in
 30 this study. Steady state is determined by taking a linear regression for all the data in the last 10% time window of the plot of $\log(J(t))$ vs. $\log(t)$, where $J(t)$ is creep compliance and t is creep time. If the slope of the linear regression is greater than 0.97, steady state is considered to be reached, then the creep test is stopped. In all

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cases in this study the slope meets the criterion within 2 hours. The steady state shear rate is determined from the slope of the linear regression of all of the data points in the last 10% time window of the plot of ϵ vs. t , where ϵ is strain. The zero-shear viscosity is determined from the ratio of the applied stress to the steady state shear rate.

In order to determine if the sample is degraded during the creep test, a small amplitude oscillatory shear test is conducted before and after the creep test on the same specimen from 0.1 to 100 rad/s. The complex viscosity values of the two tests are compared. If the difference of the viscosity values at 0.1 rad/s is greater than 5%, the sample is considered to have degraded during the creep test, and the result is discarded.

Zero-shear viscosity ratio (ZSVR) is defined as the ratio of the zero-shear viscosity (ZSV) of the branched polyethylene material to the ZSV of the linear polyethylene material at the equivalent weight average molecular weight (Mw-gpc) as shown in the Equation 18, as shown in Figure 18.

The ZSV value is obtained from creep test at 190°C via the method described above. The Mw-gpc value is determined by the conventional GPC method. The correlation between ZSV of linear polyethylene and its Mw-gpc was established based on a series of linear polyethylene reference materials. A description for the ZSV-Mw relationship can be found in the ANTEC proceeding: Karjala, Teresa P.; Sammler, Robert L.; Mangnus, Marc A.; Hazlitt, Lonnie G.; Johnson, Mark S.; Hagen, Charles M., Jr.; Huang, Joe W. L.; Reichel, Kenneth N. Detection of low levels of long-chain branching in polyolefins. Annual Technical Conference - Society of Plastics Engineers (2008), 66th 887-891.

¹H NMR method

3.26 g of stock solution is added to 0.133 g of polyolefin sample in 10 mm NMR tube. The stock solution is a mixture of tetrachloroethane- d_2 (TCE) and perchloroethylene (50:50, w:w) with 0.001M Cr^{3+} . The solution in the tube is purged with N_2 for 5 minutes to reduce the amount of oxygen. The capped sample tube is left at room temperature overnight to swell the polymer sample. The sample is dissolved at 110°C with shaking. The samples are free of the additives that may contribute to unsaturation, e.g. slip agents such as erucamide.

The 1H NMR are run with a 10 mm cryoprobe at 120°C on Bruker AVANCE 400 MHz spectrometer.

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Two experiments are run to get the unsaturation: the control and the double presaturation experiments.

For the control experiment, the data is processed with exponential window function with LB=1 Hz, baseline was corrected from 7 to -2 ppm. The signal from residual ^1H of TCE is set to 100, the integral I_{total} from -0.5 to 3 ppm is used as the signal from whole polymer in the control experiment. The number of CH_2 group, NCH_2 , in the polymer is calculated as following:

$$\text{NCH}_2 = I_{\text{total}}/2$$

For the double presaturation experiment, the data is processed with exponential window function with LB=1 Hz, baseline was corrected from 6.6 to 4.5 ppm. The signal from residual ^1H of TCE is set to 100, the corresponding integrals for unsaturations (I_{vinylene} , $I_{\text{trisubstituted}}$, I_{vinyl} and $I_{\text{vinylidene}}$) were integrated based on the region shown in Figure 2. The number of unsaturation unit for vinylene, trisubstituted, vinyl and vinylidene are calculated:

$$\begin{aligned} \text{N}_{\text{vinylene}} &= I_{\text{vinylene}}/2 \\ \text{N}_{\text{trisubstituted}} &= I_{\text{trisubstituted}} \\ \text{N}_{\text{vinyl}} &= I_{\text{vinyl}}/2 \\ \text{N}_{\text{vinylidene}} &= I_{\text{vinylidene}}/2 \end{aligned}$$

The unsaturation unit/ 1,000,000 carbons is calculated as following:

$$\begin{aligned} \text{N}_{\text{vinylene}}/1,000,000\text{C} &= (\text{N}_{\text{vinylene}}/\text{NCH}_2)*1,000,000 \\ \text{N}_{\text{trisubstituted}}/1,000,000\text{C} &= (\text{N}_{\text{trisubstituted}}/\text{NCH}_2)*1,000,000 \\ \text{N}_{\text{vinyl}}/1,000,000\text{C} &= (\text{N}_{\text{vinyl}}/\text{NCH}_2)*1,000,000 \\ \text{N}_{\text{vinylidene}}/1,000,000\text{C} &= (\text{N}_{\text{vinylidene}}/\text{NCH}_2)*1,000,000 \end{aligned}$$

The requirement for unsaturation NMR analysis includes: level of quantitation is $0.47 \pm 0.02/1,000,000$ carbons for Vd2 with 200 scans (less than 1 hour data acquisition including time to run the control experiment) with 3.9 wt% of sample (for

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Vd2 structure, see Macromolecules, vol. 38, 6988, 2005), 10 mm high temperature cryoprobe. The level of quantitation is defined as signal to noise ratio of 10.

The chemical shift reference is set at 6.0 ppm for the ^1H signal from residual proton from TCT-d2. The control is run with ZG pulse, TD 32768, NS 4, DS 12, SWH 10,000 Hz, AQ 1.64s, D1 14s. The double presaturation experiment is run with a modified pulse sequence , O1P 1.354 ppm, O2P 0.960 ppm, PL9 57db, PL21 70 db, TD 32768, NS 200, DS 4, SWH 10,000 Hz, AQ 1.64s, D1 1 s, D13 13s. The modified pulse sequences for unsaturation with Bruker AVANCE 400 MHz spectrometer are shown in Figure 21.

Gel Content

Gel content is determined in accordance to ASTM D-2765-01 Method A in xylene. The sample is cut to required size using a razor blade.

Film Testing Conditions

The following physical properties are measured on the films produced:

- Total (Overall), Surface and Internal Haze: Samples measured for internal haze and overall haze are sampled and prepared according to ASTM D-1003. Internal haze was obtained via refractive index matching using mineral oil on both sides of the films. A Hazegard Plus (BYK-Gardner USA; Columbia, MD) is used for testing. Surface haze is determined as the difference between overall haze and internal haze (Haze=Internal Haze + Surface Haze). Surface haze tends to be related to the surface roughness of the film, where surface increases with increasing surface roughness. The surface haze to internal haze ratio is the surface haze value divided by the internal haze value ($S/I = \text{Surface Haze} / \text{Internal Haze}$);
- 45° Gloss: ASTM D-2457;
- MD and CD Elmendorf Tear Strength: ASTM D-1922. The reported data is normalized with respect to the film thickness in mil;
- MD and CD Tensile Strength: ASTM D-882;
- Dart Impact Strength: ASTM D-1709; and

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- Puncture Strength: Puncture is measured on a Instron Model 4201 with Sintech Testworks Software Version 3.10. The specimen size is 6" x 6" and 4 measurements are made to determine an average puncture value. The film is conditioned for 40 hours after film production and at least 24 hours in an ASTM controlled laboratory. A 100 lb load cell is used with a round specimen holder 12.56" square. The puncture probe is a ½" diameter polished stainless steel ball with a 7.5" maximum travel length. There is no gauge length; the probe is as close as possible to, but not touching, the specimen. The crosshead speed used is 10"/minute. The thickness is measured in the middle of the specimen. The thickness of the film, the distance the crosshead traveled, and the peak load are used to determine the puncture by the software. The puncture probe is cleaned using a "Kim-wipe" after each specimen.

Unless otherwise stated, implicit from the context or conventional in the art, all parts and percentages are based on weight.

- All applications, publications, patents, test procedures, and other documents cited, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with the disclosed compositions and methods and for all jurisdictions in which such incorporation is permitted.

We claim:

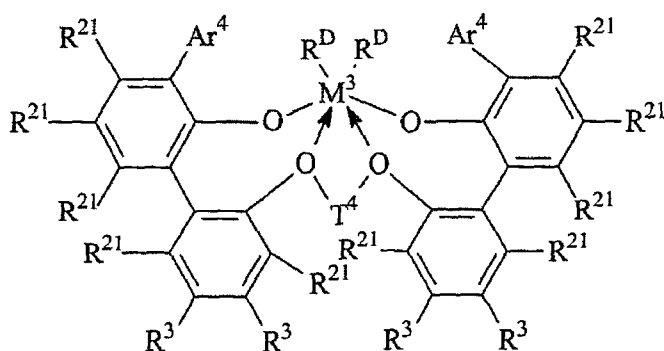
1. An ethylene-based polymer composition characterized by a Comonomer
Distribution Constant in the range of from greater than 45 to less than 400,
5 wherein the composition has less than 120 total unsaturation unit/1,000,000C.
2. The polymer composition of Claim 1 wherein the composition comprises from
0.01 to 3 long chain branches/1000 carbons.
- 10 3. The polymer composition of claim 1 having a ZSVR of at least 2.
4. The polymer of claim 3 further characterized by comprising less than 20
vinylidene unsaturation unit/1,000,000C.
- 15 5. The polymer composition of Claim 1 wherein the composition has a bimodal
molecular weight distribution.
6. The polymer composition of Claim 1 wherein the composition has a multi-
modal MWD.
- 20 7. A fabricated article comprising the composition of Claim 1.
8. The polymer composition of Claim 1 further comprising a single DSC melting
peak.
- 25 9. A thermoplastic formulation comprising the composition of Claim 1 and at
least one natural or synthetic polymer.
10. The composition of Claim 1, wherein said composition has been at least
30 partially cross-linked (at least 5% gel).
11. The composition of Claim 1, wherein the composition has a comonomer
distribution profile comprising a mono or bimodal distribution in the
temperature range of from 35°C to 120°C, excluding purge.

12. The polymer composition of Claim 1 comprising Mw from about 17,000 to about 220,000.

5 13. A polymerization process comprising:

(A) polymerizing ethylene and optionally one or more α -olefins in the presence of a first catalyst to form a semi-crystalline ethylene-based polymer in a first reactor or a first part of a multi-part reactor; and

(B) reacting freshly supplied ethylene and optionally one or more α -olefins in
 10 the presence of a second catalyst comprising an organometallic catalyst thereby forming an ethylene-based polymer composition of Claim 1 in at least one other reactor or a later part of said multi-part reactor, wherein the catalyst of (A) and (B) can be the same or different and each is a metal complex of a polyvalent aryloxyether corresponding to the formula:



15 where M^3 is Ti, Hf or Zr, preferably Zr;

Ar^4 is independently in each occurrence a substituted C_{9-20} aryl group, wherein the substituents, independently in each occurrence, are selected from the group consisting of alkyl; cycloalkyl; and aryl groups; and halo-, trihydrocarbylsilyl- and
 20 halohydrocarbyl- substituted derivatives thereof, with the proviso that at least one substituent lacks co-planarity with the aryl group to which it is attached;

T^4 is independently in each occurrence a C_{2-20} alkylene, cycloalkylene or cycloalkenylene group, or an inertly substituted derivative thereof;

R^{21} is independently in each occurrence hydrogen, halo, hydrocarbyl,
 25 trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or di(hydrocarbyl)amino group of up to 50 atoms not counting hydrogen;

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R^3 is independently in each occurrence hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen, or two R^3 groups on the same arylene ring together or an R^3 and an R^{21} group on the same or different arylene ring together form a divalent ligand group attached to the arylene group in two positions or join two different arylene rings together; and

R^D is independently in each occurrence halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl, diene, or poly(hydrocarbyl)silylene group.

14. The fabricated article of Claim 8 in the form of at least one film layer.