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(54) Title: POLYETHYLENE COMPOSITIONS AND FILMS

(57) Abstract: Embodiments of the present invention relate to polyethylene compositions suitable for use in making a film having a matte surface. The composition comprises a first and second polyethylene component having a specified molecular weight distribution along with other overall properties to allow for a matte surface in polymer films. Films made from the polyethylene composition can have a gloss of less than 10% and a total haze of greater than 60%.



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POLYETHYLENE COMPOSITIONS AND FILMS

Technical Field

This disclosure relates to polyethylene compositions, to films having a matte surface
5 comprising polyethylene compositions, and to articles, such as labels and packages, comprising
films having a matte surface.

Introduction

As global interest solidifies in reducing packaging waste and making flexible packaging
more sustainable, there is an increasing amount of effort to develop materials and technologies
10 that would enhance the sustainability of flexible packaging. Flexible packaging film structures
are often formed of multiple types of polymeric materials including, for example, polyethylene,
polypropylene, ethylene vinyl alcohol, polyethylene terephthalate, polyamide and others. Such
materials are typically combined to achieve a balance of properties that are beyond the reach
of a single material type. However, due to the dissimilarity of these materials, the final package
15 is typically not easy to recycle and a blend of materials can also create issues with process
control. Thus, there is also a movement towards single component structures (e.g., all
polyethylene structures) to improve the recyclability profile and to reduce process control
issues. In the case of all polyethylene structures, for example, certain performance metrics (e.g.,
mechanical properties) will need to be enhanced to maintain the level of performance expected
20 of these structures when formed from different polymeric materials. Thus, new polyethylene
resin and processing technologies are needed to bridge performance deficiencies of polyolefins
relative to other material types.

One area for new polyethylene composition technologies in the packaging space is
films having a matte surface. A matte surface can be defined in terms of optical properties with
25 lower gloss and higher haze values as discussed herein. A common approach to obtaining a
matte surface is to use a blend of polymers or inorganic fillers. For example, some methods
use matte oriented polyethylene terephthalate and polypropylene to deliver a matte surface
whereas other methods employ matte coatings. In addition to incorporating non-polyethylene
polymers, these methods introduce additional process(es) to provide matte finish. Coextrusion
30 of a polyethylene based matte layer is a more streamlined process, but coextrusion still typically
relies on blending non-polyethylene components like polypropylene, cyclic olefinic
copolymers, and micron sized inorganic particles in a layer to achieve matte finish.
Furthermore, even when polyethylene resin designs are used, certain polyethylene resins are

prone to dusting (i.e., powder formation), which, for example, can lead to contamination of film fabrication equipment.

Accordingly, there remains a need for polyethylene compositions that can achieve a matte surface in polymer films, can assist in delivering recyclable packaging, and can be processed without the need to be mixed with other polymers and without significant dusting.

Summary

The present invention provides polyethylene compositions that can be extruded to form films that have a matte surface.

In a first aspect, a polyethylene composition is disclosed. The polyethylene composition according to embodiments disclosed herein comprises from 30 to 70 wt.% of a first polyethylene component having a molecular weight distribution (Mw/Mn) of 1.50 to 2.50; from 30 to 70 wt.% of a second polyethylene component having a molecular weight distribution (Mw/Mn) of 1.50 to 2.50; wherein the wt.% of the first polyethylene component and second polyethylene component is based on the total weight of the polyethylene composition, wherein the first polyethylene component has a higher weight average molecular weight than the second polyethylene component, wherein the polyethylene composition has a density of 0.950 to 0.960 g/cm³, a melt index (I₂) of 0.5 to 6.0 g/10 min, a molecular weight distribution (Mw/Mn) of 2.0 to 6.0, and a Mz of 100,000 to 500,000 g/mol.

In a second aspect, a film is disclosed. The film according to embodiments disclosed herein comprises the polyethylene composition of the first aspect of the invention. A label or package comprising the film is also disclosed.

As discussed below, the present invention also provides articles, such as labels and packages, formed from any of the inventive polyethylene composition or films disclosed herein.

These and other embodiments are described in more detail in the Detailed Description.

Detailed Description

Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight, all temperatures are in °C, and all test methods are current as of the filing date of this disclosure.

The term “composition,” as used herein, refers to a mixture of materials which comprises the composition, as well as reaction products and decomposition products formed from the materials of the composition.

“Polymer” means a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term interpolymers as defined hereinafter. Trace amounts of impurities (for example, catalyst residues) may be incorporated into and/or within the polymer. A polymer may be a single polymer, a polymer blend or a polymer mixture, including mixtures of polymers that are formed *in situ* during polymerization.

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 thus includes copolymers (employed to refer to polymers prepared from two different types of monomers), and polymers prepared from more than two different types of monomers.

The terms “olefin-based polymer” or “polyolefin”, as used herein, refer to a polymer that comprises, in polymerized form, a majority amount of olefin monomer, for example ethylene or propylene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term, “ethylene/ α -olefin interpolymer,” as used herein, refers to an interpolymer that comprises, in polymerized form, a majority amount (>50 mol %) of units derived from ethylene monomer, and the remaining units derived from one or more α -olefins. Typical α -olefins used in forming ethylene/ α -olefin interpolymers are C₃-C₁₀ alkenes.

The term, “ethylene/ α -olefin copolymer,” as used herein, refers to a copolymer that comprises, in polymerized form, a majority amount (>50 mol %) of ethylene monomer, and an α -olefin, as the only two monomer types.

The term “ α -olefin”, as used herein, refers to an alkene having a double bond at the primary or alpha (α) position.

“Polyethylene” or “ethylene-based polymer” shall mean polymers comprising a majority amount (>50 mol %) of units which have been derived from ethylene monomer. This includes polyethylene homopolymers, ethylene/ α -olefin interpolymers, and ethylene/ α -olefin copolymers. Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); Medium Density Polyethylene (MDPE); High Density Polyethylene (HDPE); Enhanced Polyethylene; polyethylene elastomers; and polyethylene plastomers. These polyethylene materials are

generally known in the art; however, the following descriptions may be helpful in understanding the differences between some of these different polyethylene resins.

The term “LDPE” may also be referred to as “high pressure ethylene polymer” or “highly branched polyethylene” and is defined to mean that the polymer is partly or entirely
5 homo-polymerized or copolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators, such as peroxides (see for example US 4,599,392, which is hereby incorporated by reference). LDPE resins typically have a density in the range of 0.916 to 0.935 g/cm³.

The term “LLDPE”, includes both resin made using the traditional Ziegler-Natta
10 catalyst systems and chromium-based catalyst systems as well as single-site catalysts, including, but not limited to, bis-metallocene catalysts (sometimes referred to as “m-LLDPE”), constrained geometry catalysts (CGC), and molecular catalysts. Resins include linear, substantially linear, or heterogeneous polyethylene copolymers or homopolymers. LLDPEs contain less long chain branching than LDPEs and includes the substantially linear
15 ethylene polymers which are further defined in U.S. Patent 5,272,236, U.S. Patent 5,278,272, U.S. Patent 5,582,923 and US Patent 5,733,155; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698; and/or blends thereof (such as those disclosed in US 3,914,342 or US
20 5,854,045). The LLDPEs can be made via gas-phase, solution-phase or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

The term “MDPE” refers to polyethylenes having densities from 0.926 to 0.940 g/cm³. “MDPE” is typically made using chromium or Ziegler-Natta catalysts or using single-
25 site catalysts including, but not limited to, bis-metallocene catalysts, constrained geometry catalysts, and molecular catalysts, and typically have a molecular weight distribution (“MWD”) greater than 2.5.

The term “HDPE” refers to polyethylenes having densities greater than about 0.940 g/cm³ and up to about 0.970 g/cm³, which are generally prepared with Ziegler-Natta catalysts,
30 chrome catalysts or single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

The term “ULDPE” refers to polyethylenes having densities of 0.880 to 0.912 g/cm³, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts, or single-site

catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

"Polyethylene plastomers/elastomers" are substantially linear, or linear, ethylene/ α -olefin copolymers containing homogeneous short-chain branching distributions comprising units derived from ethylene and units derived from at least one C₃–C₁₀ α -olefin comonomer, or at least one C₄–C₈ α -olefin comonomer, or at least one C₆–C₈ α -olefin comonomer.

Polyethylene plastomers/elastomers have a density from 0.870 g/cm³, or 0.880 g/cm³, or 0.890 g/cm³ to 0.900 g/cm³, or 0.902 g/cm³, or 0.904 g/cm³, or 0.909 g/cm³, or 0.910 g/cm³, or 0.917 g/cm³. Nonlimiting examples of polyethylene plastomers/ elastomers include AFFINITY™ plastomers and elastomers (available from The Dow Chemical Company), EXACT Plastomers (available from ExxonMobil Chemical), Tafmer (available from Mitsui), Nexlene™ (available from SK Chemicals Co.), and Lucene (available LG Chem Ltd.).

"Blend", "polymer blend" and like terms mean a composition of two or more polymers. Such a blend may or may not be miscible. Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and any other method known in the art. Blends are not laminates, but one or more layers of a laminate may contain a blend. Such blends can be prepared as dry blends, formed *in situ* (e.g., in a reactor), melt blends, or using other techniques known to those of skill in the art.

The term "in adhering contact" and like terms mean that one facial surface of one layer and one facial surface of another layer are in touching and binding contact to one another such that one layer cannot be removed from the other layer without damage to the interlayer surfaces (i.e., the in-contact facial surfaces) of both layers.

The terms "comprising," "including," "having," and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step or procedure not specifically delineated or listed.

The present invention relates to a polyethylene composition. The polyethylene composition comprises a first polyethylene component and a second polyethylene component. The first polyethylene component and second polyethylene component can be a dry blend of polymers, melt blend of polymers, or in reactor blend of polymers. In some embodiments, the polyethylene composition is formed in a single reactor or in a dual reactor such as a dual loop reactor. The first polyethylene component and the second polyethylene component are not the same or identical. The first polyethylene component has a higher weight average molecular weight (Mw) than the second polyethylene component. The Mw of each component can be measured in accordance with the test methods below.

The polyethylene composition has a density of 0.950 to 0.960 g/cm³. In some embodiments, the polyethylene composition has a density lower limit of 0.950, 0.951, 0.952, 0.953, 0.954, 0.955, 0.956, 0.957, 0.958, or 0.959 g/cm³ and an upper limit of 0.951, 0.952, 0.953, 0.954, 0.955, 0.956, 0.957, 0.958, 0.959, or 0.960 g/cm³. The polyethylene composition has a melt index (I₂) of 0.5 to 6.0 g/10 min. In some embodiments, the polyethylene composition has a melt index (I₂) of a lower limit of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, or 5.5 g/10 min and an upper limit of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 or 6.0 g/10 min. The polyethylene composition has a molecular weight distribution (Mw/Mn) of 2.0 to 6.0. In some embodiments, the polyethylene composition has a molecular weight distribution (Mw/Mn) of a lower limit of 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, or 5.5 and an upper limit of 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, or 6.0. The polyethylene composition has a Mz of 100,000 to 500,000 g/mol. In some embodiments, the polyethylene composition has a Mz of lower limit of 100,000, 150,000, 200,000, 250,000, 300,000, 350,000, 400,000 or 450,000 g/mol and an upper limit of 150,000, 200,000, 250,000, 300,000, 350,000, 400,000, 450,000 or 500,000 g/mol. The characteristics of the polyethylene composition can be measured in accordance with the test methods below.

The polyethylene composition comprises from 30 to 70 wt.% of a first polyethylene component, based on the total weight of the polyethylene composition. In some embodiments, the polyethylene composition comprises from 30 to 70 wt.%, or 33 to 65 wt.% or 33 to 66 wt.%, or 30 to 40 wt.%, or 55 to 65 wt.% of the first component, based on the total weight of the polyethylene composition. The first polyethylene component has a molecular weight distribution (Mw/Mn) of 1.50 to 2.50. In some embodiments, the first polyethylene component has a molecular weight distribution of lower limit of 1.60, 1.70, 1.80, 1.90, 2.00, 2.10, 2.20, 2.30, or 2.40 to an upper limit of 2.50, 2.40, 2.30, 2.20, 2.10, 2.00, 1.90, 1.80, 1.70, or 1.60.

The molecular weight distribution (Mw/Mn) of the first component can be measured in accordance with the test methods described below.

The first polyethylene component has a Mw greater than the second polyethylene component. In some embodiments, the first polyethylene component has a Mw of greater than 80,000 g/mol, or greater than 100,000 g/mol, or greater than 140,000 g/mol, or greater than 150,000 g/mol, or greater than 180,000 g/mol, or greater than 200,000 g/mol, or greater than 210,000 g/mol, or greater than 230,000 g/mol, or greater than 250,000 g/mol. In some embodiments, the first polyethylene component has a density lower than the density of the second polyethylene component. In some embodiments, the first polyethylene component has a density of less than 0.958 g/cm³, or less than 0.956 g/cm³, or less than 0.954 g/cm³, or less than 0.952 g/cm³, or less than 0.950 g/cm³, or less than 0.948 g/cm³, or from 0.940 to 0.958 g/cm³, or from 0.942 to 0.955 g/cm³, or from 0.944 to 0.953 g/cm³. The density of each component can be measured in accordance with the test methods below.

The polyethylene composition comprises from 30 to 70 wt.% of a second polyethylene component, based on the total weight of the polyethylene composition. In some embodiments, the polyethylene composition comprises from 30 to 70 wt.%, or 33 to 65 wt.% or 33 to 66 wt.%, or 30 to 40 wt.%, or 55 to 65 wt.% of the second component, based on the total weight of the polyethylene composition. The second polyethylene component has a molecular weight distribution (Mw/Mn) of 1.50 to 2.50. In some embodiments, the second polyethylene component has a molecular weight distribution of lower limit of 1.60, 1.70, 1.80, 1.90, 2.00, 2.10, 2.20, 2.30, or 2.40 to an upper limit of 2.50, 2.40, 2.30, 2.20, 2.10, 2.00, 1.90, 1.80, 1.70, or 1.60. The molecular weight distribution (Mw/Mn) of the second component can be measured in accordance with the test methods described below.

The second polyethylene component has a Mw lower than the first polyethylene component. In some embodiments, the second polyethylene component has a Mw of less than 80,000 g/mol, or less than 70,000 g/mol, or less than 60,000 g/mol, or less than 50,000 g/mol, or less than 40,000 g/mol, or less than 30,000 g/mol. In some embodiments, the second polyethylene component has a density higher than the density of the first polyethylene component. In some embodiments, the second polyethylene component has a density of greater than 0.958 g/cm³, or greater than 0.960 g/cm³, or greater than 0.962 g/cm³, or greater than 0.964 g/cm³, or greater than 0.966 g/cm³, or greater than 0.968 g/cm³, or from 0.958 to 0.974 g/cm³, or from 0.959 to 0.972 g/cm³, or from 0.960 to 0.971 g/cm³. The density of each component can be measured in accordance with the test methods below.

Films

The present invention also relates to films comprising the polyethylene composition disclosed herein and having at least one matte surface and to articles, labels, and packages formed from such films. The matte surface can provide a desirable appearance. In some
5 embodiments, a film comprises the polyethylene composition. In some embodiments, the film comprises an outer layer, wherein the outer layer comprises the polyethylene composition according to embodiments disclosed herein. The film can be a blown film, cast film, oriented film, or cast-stretch film. In one embodiment, the film is a blown film. In some embodiments, the outer layer of the film comprises greater than 50 wt.%, greater than 60 wt.%, greater than
10 70 wt.%, greater than 80 wt.%, greater than 90 wt.%, greater than 95 wt.%, greater than 98 wt.%, greater than 99 wt.%, or greater than 99.5 wt.% of the polyethylene composition disclosed herein.

In some embodiments, the film has a gloss of less than 10%, or less than 9% or less than 8%, or less than 7%. The gloss of the film can be measured in accordance with the test
15 methods described below. In some embodiments, the film has a total haze greater than 60% or greater than 70% or greater than 80%. The total haze of the film can be measured in accordance with the test methods described below. In some embodiments, the film has an internal haze of greater than 8%, or greater than 10%, or greater than 12% or greater than 14% or greater than 16%. The internal haze of the film can be measured in accordance with the test methods
20 described below. In some embodiments, the film comprises greater than 95 wt.%, or greater than 97 wt.%, or greater than 99 wt.%, or greater than 99.9 wt.% polyethylene, based on the total polymer content of the film. In some embodiments, the film is void of polymers other than polyethylene.

The present invention also provides articles, such as labels and packages, formed from
25 any of the inventive films disclosed herein.

The outer layer in a film can provide a matte surface. As used herein, the term “matte surface” generally refers to a surface with a dull appearance, as opposed to a glossy appearance. A matte surface as discussed herein has one or both of (1) a gloss of less than 10%, and (2) a haze of greater than 60%.

In some embodiments, a film comprises an outer layer comprising the polyethylene composition according to embodiments disclosed herein and an inner layer in adhering contact with the outer layer. In embodiments where an inner layer is present, the inner layer can comprise a LDPE, LLDPE, MDPE, HDPE, or a combination thereof. Suitable LLDPEs for use
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in the inner layer include DOWLEX grades commercially available from The Dow Chemical Company. In some embodiments, where an inner layer is present, the inner layer comprises a low density polyethylene (e.g., an LDPE or LLDPE) having a density of 0.919 to 0.940 g/cm³. All individual values and subranges of 0.919 to 0.940 g/cm³ are included herein and disclosed
5 herein; for example, the density of the low density polyethylene can be from a lower limit of 0.919, 0.920, 0.922, 0.925, 0.927, 0.929, or 0.930 g/cm³ to an upper limit of 0.925, 0.930, 0.935, or 0.940 g/cm³. In some embodiments, the low density polyethylene has a density of 0.930 to 0.940 g/cm³.

In some embodiments, the low density polyethylene has a melt index (I₂) 0.3 to 5 g/10
10 minutes. All individual values and subranges from 0.3 to 5 g/10 minutes are included herein and disclosed herein. For example, the low density polyethylene can have an I₂ from a lower limit of 0.3, 0.5, 0.7, 0.9, 1.0, 1.2, 1.5, 1.8, 2.0, 2.3, 2.5, 2.7, 3.0, 3.3, or 3.5 g/10 minutes to an upper limit of 2.0, 2.5, 2.8, 3.0, 3.2, 3.5, 3.7, 4.0, 4.2, 4.5, 4.8, or 5 g/10 minutes. For example, the low density polyethylene can have an I₂ of 2.5 to 4.0 g/10 minutes.

15 Examples of low density polyethylenes that can be used in the inner layer in some embodiments include DOWTM low density polyethylenes (LDPE) commercially available from The Dow Chemical Company, such as DOWTM LDPE 525E, DOWTM LDPE 410E, DOWTM LDPE 421E, DOWTM LDPE 545E, DOWTM LDPE 555E, and DOWTM LDPE 515E, and DOWLEXTM LLDPE resins commercially available from The Dow Chemical Company.

20 Other Layers

Films of the present invention can comprise a variety of other layers in addition to an outer layer and an inner layer. The number of layers in the film can depend on a number of factors including, for example, the desired properties of the film, the end use application, the desired thickness of the film, and others. For example, the other layers when the film is to be
25 used in package may be different from the other layers used when the film is to be used as a label. Examples of different layers that can be used in various embodiments are discussed further herein. Films of the present invention comprise up to 13 layers in some embodiments. In various embodiments, the film comprises 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13 layers.

In some embodiments, a film of the present invention comprises a second outer layer
30 which is a sealant layer. The sealant layer can be used to form an article or package by using the sealant layer to adhere the film to another film, to a laminate, or to itself. In some embodiments, the sealant layer can comprise any resins known to those having ordinary skill in the art to be useful as a sealant layer. Examples of polymers that can be used to form a

sealant layer in some embodiments of the present invention include, without limitation, LDPE (e.g., DOW™ LDPE and AGILITY™ LDPE commercially available from The Dow Chemical Company), LLDPE (e.g., DOWLEX™ LLDPE resins commercially available from The Dow Chemical Company), polyolefin plastomers or elastomers (e.g., AFFINITY™ plastomers and elastomers commercially available from The Dow Chemical Company), ethylene vinyl acetate copolymers (e.g., ELVAX™ ethylene vinyl acetate copolymers commercially available from The Dow Chemical Company) and ionomers of ethylene acid copolymers (e.g., SURLYN™ ionomers commercially available from The Dow Chemical Company).

In some embodiments, the film comprises a second outer layer that provides a second matte surface and comprises the polyethylene composition according to embodiments disclosed herein.

In some embodiments, depending on the desired use or requirements of the film, the film can comprise other layers such as barrier layers. For example, for some uses, it may be desirable for the film to provide a barrier to moisture, light, aroma/odor, and/or oxygen transmission. Such barrier layers can comprise, for example, polymers used in barrier layers as known to those of skill in the art. In such embodiments, an inner layer of the film comprises ethylene vinyl alcohol copolymer. In some such embodiments, the film comprises 30 weight percent or less ethylene vinyl alcohol copolymer based on the total weight of the film. In some embodiments, the film comprises 20 weight percent or less ethylene vinyl alcohol copolymer based on the total weight of the film. In some embodiments, the film comprises 10 weight percent or less ethylene vinyl alcohol copolymer based on the total weight of the film. In some embodiments, the film comprises less than 5% by weight ethylene vinyl alcohol copolymer and polyamide based on the total weight of the film.

In embodiments comprising an inner layer having ethylene vinyl alcohol copolymer, one or more tie layers may be included in the film to adhere the barrier layer(s) other layers as known to those of skill in the art based on the teachings herein. In general, a wide variety of tie layer compositions can be used to form a tie layer as known to those of skill in the art based on the teachings herein.

In some embodiments, barrier properties may not be as important for the film. In some such embodiments, the film may comprise less than 0.5 weight percent ethylene vinyl alcohol copolymer based on the total weight of the film. In some embodiments, the film comprises less than 0.1 weight percent ethylene vinyl alcohol copolymer based on the total weight of the

film. In some embodiments, the film is free of ethylene vinyl alcohol copolymer and polyamide.

In some embodiments, a film of the present invention has a total thickness of at least 30 microns. In some embodiments, the film has a thickness of up to 90 microns. In some
5 embodiments, the film has a thickness from 30 microns to 90 microns.

Films of the present invention can exhibit one or more desirable properties. As discussed elsewhere, the films of the present invention have a matte surface. Films can be coextruded as blown films or cast films using techniques known to those of skill in the art based on the teachings herein. In particular, based on the compositions of the different film layers
10 disclosed herein, blown film manufacturing lines and cast film manufacturing lines can be configured to coextrude films of the present invention in a single extrusion step using techniques known to those of skill in the art based on the teachings herein.

Labels

Embodiments of the present invention also comprise labels formed from or
15 incorporating films of the present invention. Such labels can be made from the inventive polyethylene compositions using techniques known to those having ordinary skill in the art based on the teachings herein.

Packages

Embodiments of the present invention also comprise packages formed from or
20 incorporating polyethylene compositions of the present invention. Such packages can be made from the inventive polyethylene compositions and films comprising such compositions using techniques known to those having ordinary skill in the art based on the teachings herein.

Examples of such packages can include flexible packages, pouches, stand-up pouches, and pre-made packages or pouches. In some embodiments, films of the present invention can
25 be used for food packages. Examples of food that can be included in such packages include meats, cheeses, cereal, nuts, juices, sauces, and others. Such packages can be formed using techniques known to those of skill in the art based on the teachings herein and based on the particular use for the package (e.g., type of food, amount of food, etc.).

TEST METHODS

Unless otherwise indicated herein, the following analytical methods are used in
30 describing aspects of the present invention:

Melt Index

Melt index I₂ (or I2) is measured in accordance to ASTM D-1238 (method B) at 190°C and at 2.16 kg. Their values are reported in g/10 min.

Density

- 5 Samples for density measurement are prepared according to ASTM D4703 Annex A.1 Proc C. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

Haze

- 10 Haze is measured according to ASTM D 1003. A Hazegard Plus (BYK-Gardner USA; Columbia, MD) was used for testing. For each test, 5 samples were examined, and an average was reported. For Internal Haze, a small amount of mineral oil is placed on both surfaces of the film and the oil spread evenly using a cotton swab. The sample is then placed as close as possible to the haze port and a reading taken.

Gloss

- 15 Gloss at an angle of 45° was measured according to ASTM D2457 on a BYK-Gardner (Columbia, MD) micro-gloss 45 degree gloss meter (Columbia, MD). For testing the specimens are placed in a telescoping hoop to ensure there are no wrinkles/folds in the film. The specimen is placed on a black background and the gloss meter placed on the specimen and a reading taken. Five replicates are measured per sample.

20 **Gel Permeation Chromatography (GPC) and Deconvolution Method – Density, Mw, and Mw/Mn of Each Component**

- The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 25 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The 30 injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

 Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and

were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (EQ1)$$

where M is the molecular weight, A has a value of 0.4028 and B is equal to 1.0.

A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

The calculations of $M_{n(GPC)}$, $M_{w(GPC)}$, and $M_{z(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ 2)$$

$$Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ 3)$$

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ 4)$$

In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate_(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV_(FM Sample)) to that of the decane peak within the narrow standards calibration (RV_(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate_(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

$$Flowrate_{(effective)} = Flowrate_{(nominal)} * (RV_{(FM Calibrated)} / RV_{(FM Sample)}) \quad (EQ5)$$

Deconvolution of GPC Chromatogram – The fitting of the chromatogram into a high molecular weight (HMW) and low molecular weight (LMW) component fraction was accomplished using a Flory distribution which was broadened with a normal distribution function as follows: For the log M axis, 601 equally-spaced Log(M) points, spaced by 0.01, were established between 2 and 8 representing the molecular weight range between 100 and

100,000,000 where Log is the logarithm function to the base 10. At any given Log (M), the population of the Flory distribution was in the form of Eq. 6:

$$dW_f/d\text{Log}M = \left(\frac{2}{M_w}\right)^3 \left(\frac{M_w}{0.868588961964}\right) M^2 e^{(-2M/M_w)} \quad \text{Eq. 6}$$

where M_w is the weight-average molecular weight of the Flory distribution and M is the specific x-axis molecular weight point, $(10^{\wedge} [\text{Log}(M)])$. The Flory distribution weight fraction was broadened at each 0.01 equally-spaced $\text{log}(M)$ index according to a normal distribution function, of width expressed in $\text{Log}(M)$, σ ; and current M index expressed as $\text{Log}(M)$, μ .

$$f_{(\text{Log}M, \mu, \sigma)} = e^{-\frac{(\text{Log}M - \mu)^2}{2\sigma^2}} \quad \text{Eq. 7}$$

It should be noted that before and after the spreading function has been applied that the area of the distribution ($dW_f / d\text{Log}M$) as a function of $\text{Log}(M)$ is normalized to unity. Two weight-fraction distributions, dW_{f1} and dW_{f2} , for LMW and HMW components or components 1 and 2 were expressed with two unique M_w target values, M_{w1} and M_{w2} and with overall component compositions A_1 and A_2 , where each composition weight% is quantified by the known reactor split in the process. Both distributions were broadened with the same width, s .

The two distributions were summed as follows:

$$dW_f/d\text{Log}M = A_1 dW_{f1}/d\text{Log}M + A_2 dW_{f2}/d\text{Log}M \quad \text{Eq. 8}$$

where: $A_1 + A_2 = 1$

The weight fraction result of the measured GPC molecular weight distribution was interpolated along 601 $\log M$ points using a 2nd-order polynomial. Microsoft Excel™ 2010 Solver was used to minimize the sum of squares of residuals for the equally-spaces range of 601 $\text{Log}M$ points between the interpolated chromatographically determined molecular weight distribution and the two broadened Flory distribution components (s_1 and s_2), weighted with their respective component compositions, A_1 and A_2 . The iteration starting values for the components are as follows:

Component 1: $M_{w1} = 20,000$, $s = 0.200$, and $A_1 =$ weight fraction of the HMW component

Component 2: $M_{w2} = 200,000$, $s = 0.200$, and $A_2 = 1 - A_1$

(Note $s_1 = s_2$ and $A_1 + A_2 = 1$)

The bounds for components 1 and 2 are such that s is constrained such that $s > 0.001$, yielding an M_w/M_n of approximately 2.00 and $s < 0.550$, yielding a M_w/M_n of approximately 5.71.

The composition, A_1 , is constrained between 0.000 and 1.000. The M_{w1} is constrained between 2,500 and 2,000,000. The composition, A_2 , is constrained between 0.000 and 1.000. The M_{w2} is constrained between 2,500 and 2,000,000. The “GRG Nonlinear” engine was selected in

Excel Solver™ and precision was set at 0.00001 and convergence was set at 0.0001. The solutions were obtained after convergence (in all cases shown, the solution converged within 60 iterations).

The density of each component was calculated from the equation below:

5 $Density = 0.955 - (0.0253573299637067 * LOG(Mw) - 0.123253224502496)$

Examples

The following materials are used:

Production of Comparative Example (CE1)

10 All raw materials (monomer and comonomer) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, Isopar-E) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied pressurized as a high purity grade and is not further purified. The reactor monomer feed stream is pressurized via a mechanical compressor to above reaction pressure. The solvent and comonomer feed is pressurized via a pump to above reaction pressure. The individual catalyst components are
15 manually batch diluted with purified solvent and pressured to above reaction pressure. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

 A single reactor system is used. The continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a
20 continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the polymerization reactor is injected into the reactor at two
25 locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through an injection stinger. The primary catalyst component feed is computer controlled to maintain the reactor monomer conversion at the specified targets. The cocatalyst component is fed based on calculated
30 specified molar ratio to the primary catalyst component. Immediately following each reactor feed injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of the reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the

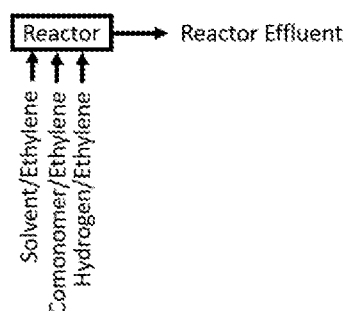
temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around the reactor loop is provided by a pump.

The reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (water) and a neutralizer added (calcium stearate). At this same reactor exit location other additives are added for polymer stabilization (typical antioxidants suitable for stabilization during extrusion and blown film fabrication like Octadecyl 3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate, Tetrakis(Methylene(3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate))Methane, and Tris(2,4-Di-Tert-Butyl-Phenyl) Phosphite).

Following catalyst deactivation, neutralization, and additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The isolated polymer melt is pelletized and collected. The non-polymer stream passes through various pieces of equipment which separate most of the ethylene which is removed from the system. Most of the solvent and unreacted comonomer is recycled back to the reactor after passing through a purification system. A small amount of solvent and comonomer is purged from the process.

The reactor stream feed data flows that correspond to the values in Table 1 used to produce the example are graphically described in Diagram A. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram.

Diagram A



Production of Comparative Example (CE4)

All raw materials (monomer, comonomer, hydrogen) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, Isopar-E) are purified with molecular sieves before introduction into the reaction environment. The hydrogen feed is pressurized by a compressor to above reaction pressure. The reactor monomer feed stream is pressurized via a compressor to above reaction pressure. The solvent and comonomer feed is pressurized via a pump to above reaction pressure. The individual catalyst components are fed to the reactor

using dedicated feed metering systems and pumps. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

5 A two-reactor system is used in a series configuration. The first continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the first reactor (solvent, monomer, comonomer, and hydrogen) is temperature controlled to maintain a single solution phase by
10 passing the feed stream through a heat exchanger. The total fresh feed to the first polymerization reactor is injected into the reactor at two locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through dedicated injectors. The primary catalyst component feed is
15 computer controlled to maintain the reactor monomer conversion at the specified target. The cocatalyst component are fed based on calculated specified molar ratios to the primary catalyst component. Following each reactor feed injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of the reactor are continuously circulated through heat exchangers responsible for removing much
20 of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around the first reactor loop is provided by a pump.

The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the first reactor and is added
25 to the second reactor. The second continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the second reactor (solvent, monomer, comonomer, and hydrogen) is
30 temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the second polymerization reactor is injected into the reactor at two locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed

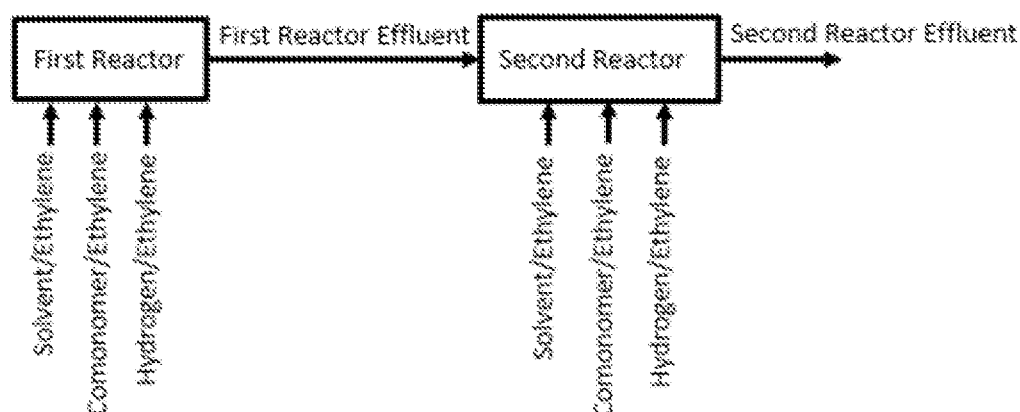
mass flow. The catalyst components are injected into the polymerization reactor through dedicated injectors. The primary catalyst component feed is computer controlled to maintain the reactor monomer conversion at the specified target. The cocatalyst component is fed based on a specified molar ratio to the primary catalyst component. Immediately following each reactor feed injection location, the streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of the second reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around the second reactor loop is provided by a pump.

The final reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (water) and a neutralizer added (calcium stearate). At this same reactor exit location other additives are added for polymer stabilization (typical antioxidants suitable for stabilization during extrusion and blown film fabrication like Octadecyl 3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate, Tetrakis(Methylene(3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate))Methane, and Tris(2,4-Di-Tert-Butyl-Phenyl) Phosphite).

Following catalyst deactivation, neutralization, and additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The isolated polymer melt is pelletized and collected. The non-polymer stream passes through various pieces of equipment which separate most of the ethylene which is removed from the system. Most of the solvent and unreacted comonomer is recycled back to the reactor after passing through a purification system. A small amount of solvent and comonomer is purged from the process.

The reactor stream feed data flows that correspond to the values in Table 1 used to produce the example are graphically described in Diagram B. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can be treated more simply as a once through flow diagram.

Diagram B



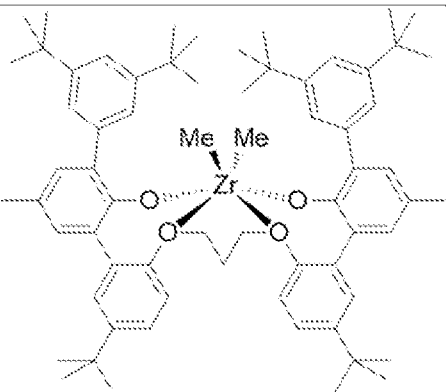
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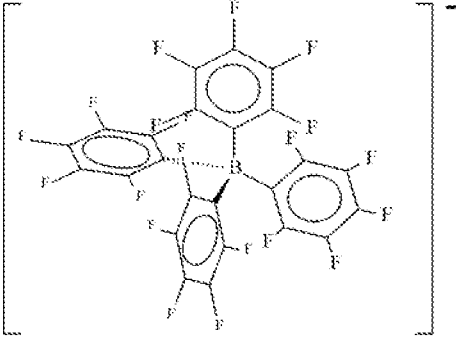
Table 1

		CE1	CE4
Reactor Configuration	Type	Dual Series	Dual Series
Comonomer type	Type	none	1-octene
First Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	3.09	5.96
First Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.000	0.007
First Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	9.05E-05	6.15E-05
First Reactor Temperature	°C	195	177
First Reactor Pressure	barg	50	35
First Reactor Ethylene Conversion	%	93.8	88.4
First Reactor Catalyst Type	Type	Cat-A	Cat-C
Catalyst Type metal for cocatalyst ratio		Ti	Zr
First Reactor Co-Catalyst 1 Type	Type	--	Co-catalyst A
First Reactor Co-Catalyst 2 Type	Type	Co-catalyst C	Co-catalyst B
First Reactor Co-Catalyst 1 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	mol/mol	--	1.2
First Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	mol/mol	12.1	10.0
First Reactor Residence Time	min	6.4	8.6
Percentage of Total Ethylene Feed to First Reactor	wt%	100.0%	48.3%
Second Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g		2.38
Second Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g		0.0009
Second Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g		6.64E-04
Second Reactor Temperature	°C		200

Second Reactor Pressure	barg		35
Second Reactor Ethylene Conversion	%		88.2
Second Reactor Catalyst Type	Type		Cat-B
Second Reactor Co-Catalyst 1 Type	Type		Co-catalyst C
Second Reactor Co-Catalyst 1 to Catalyst Molar Ratio (Al to Ti ratio)	mol/mol		4.0
Second Reactor Residence Time	min		5.5

Table 2

Cat-A	To a slurry of MgCl ₂ in ISOPAR E (as prepared according to U.S. Pat. No. 4,612,300) EADC was added and stirred for 4 hr. TiCl ₄ and VOCl ₄ were added and stirred for 1 hr. Zr(TMHD) ₄ was added and the resulting mixture was stirred for 8 hr prior to use. The pre-catalyst composition comprised a molar ratio of Mg/Al/Ti/V/Zr of 40/10/1/2/0.5.
Cat-B	The catalyst system comprised a Ziegler-Natta type catalyst. The heterogeneous Ziegler-Natta type catalyst-premix was prepared substantially according to U.S. Pat. No. 4,612,300, by sequentially adding to a volume of ISOPAR E, a slurry of anhydrous magnesium chloride in ISOPAR E, a solution of EtAlCl ₂ in heptane, and a solution of Ti(O-iPr) ₄ in heptane, to yield a composition containing a magnesium concentration of 0.20M and a ratio of Mg/Al/Ti of 40/12.5/3. The catalyst premix was contacted with a dilute solution of Et ₃ Al, in the molar Al to Ti ratio specified in Table 1, to give the active catalyst.
Cat-C	

Co-catalyst A	R_2MeNH^+ (R = hydrogenated tallow alkyl) 
Co-catalyst B	modified methyl aluminoxane
Co-catalyst C	Triethyl aluminum

Process for Making Inventive Polyethylene Compositions

All raw materials (monomer and comonomer) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, Isopar-E) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied pressurized as a high purity grade and is not further purified. The reactor monomer feed stream is pressurized via a mechanical compressor to above reaction pressure. The solvent and comonomer feed is pressurized via a pump to above reaction pressure. The individual catalyst components are manually batch diluted with purified solvent and pressured to above reaction pressure. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

A two-reactor system is used in a series configuration. The first continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer (if used), hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the first reactor (solvent, monomer, comonomer – if used, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the first polymerization reactor is injected into the reactor at three locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving one third of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor at two different locations with similar reactor volumes between each injection location. The primary catalyst component feed is computer controlled

to maintain the reactor monomer conversion at the specified target. The cocatalyst components are fed based on calculated specified molar ratios to the primary catalyst component. Immediately following each reactor feed or catalyst injection location, the streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of the reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around each reactor loop is provided by a pump.

The second continuous solution polymerization reactor consists of a liquid full, non-adiabatic, isothermal, circulating, loop reactor which mimics a continuously stirred tank reactor (CSTR) with heat removal. Independent control of all fresh solvent, monomer, comonomer (if used), hydrogen, and catalyst component feeds is possible. The total fresh feed stream to the second reactor (solvent, monomer, comonomer – if used, and hydrogen) is temperature controlled to maintain a single solution phase by passing the feed stream through a heat exchanger. The total fresh feed to the polymerization reactor is injected into the reactor at two locations with approximately equal reactor volumes between each injection location. The fresh feed is controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through injection stingers. The primary catalyst component feed is computer controlled to maintain the reactor monomer conversion at the specified target. The boron containing cocatalyst component is fed based on calculated specified molar ratio to the primary catalyst component, and the Al containing cocatalyst component is fed to target a specified concentration in the reactor. Immediately following each reactor feed injection location, the streams are mixed with the circulating polymerization reactor contents with static mixing elements. The contents of each reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining an isothermal reaction environment at the specified temperature. Circulation around each reactor loop is provided by a pump.

The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the first reactor and is added to the second reactor.

The final reactor effluent enters a zone where it is deactivated with the addition of and reaction with a suitable reagent (water). At this same reactor exit location other additives are

added for polymer stabilization (typical antioxidants suitable for stabilization during extrusion and blown film fabrication like Octadecyl 3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate, Tetrakis(Methylene(3,5-Di-Tert-Butyl-4-Hydroxyhydrocinnamate))Methane, and Tris(2,4-Di-Tert-Butyl-Phenyl) Phosphite).

5 Following catalyst deactivation and additive addition, the reactor effluent enters a devolatilization system where the polymer is removed from the non-polymer stream. The isolated polymer melt is pelletized and collected. The non-polymer stream passes through various pieces of equipment which separate most of the ethylene which is removed from the system. Most of the solvent and unreacted comonomer is recycled back to the reactor after
10 passing through a purification system. A small amount of solvent and comonomer is purged from the process.

 The reactor stream feed data flows that correspond to the values in Table 3 used to produced the example are graphically described in Diagram 3. The data are presented such that the complexity of the solvent recycle system is accounted for and the reaction system can
15 be treated more simply as a once through flow diagram.

Diagram 3

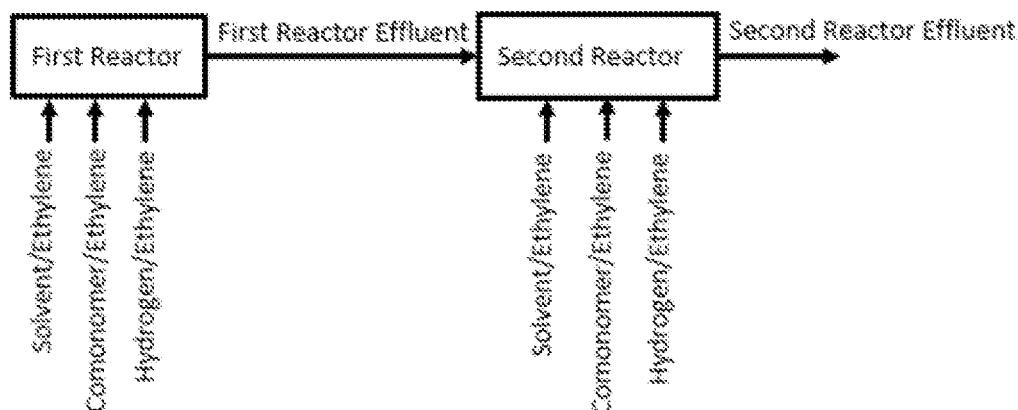
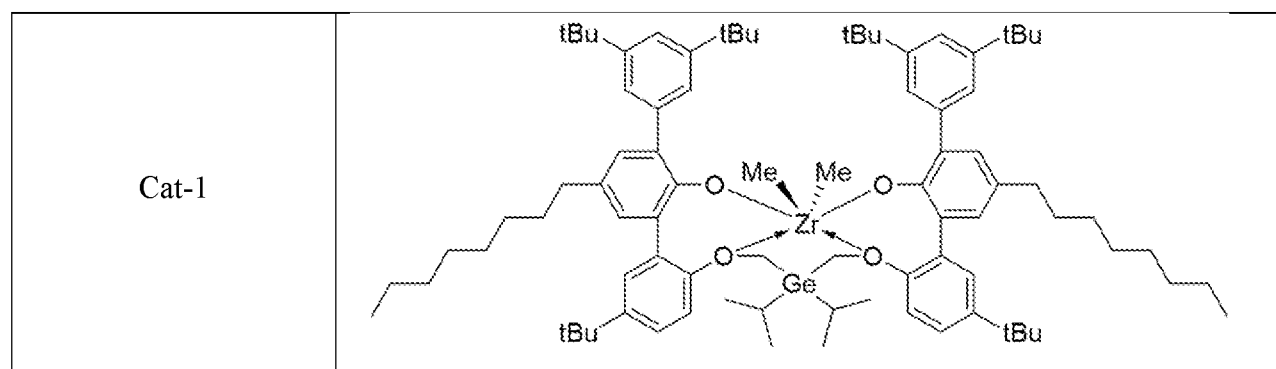


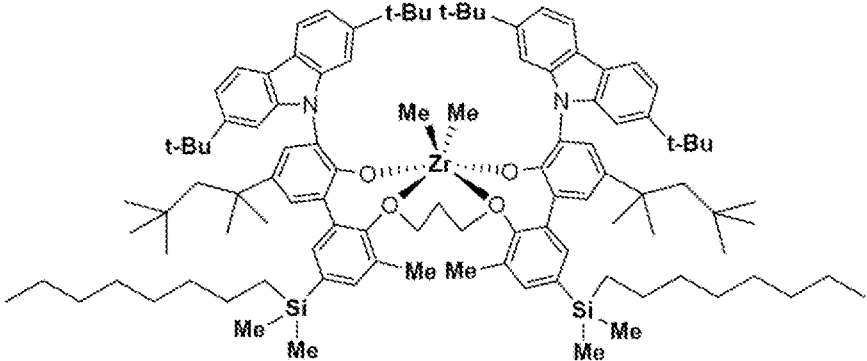
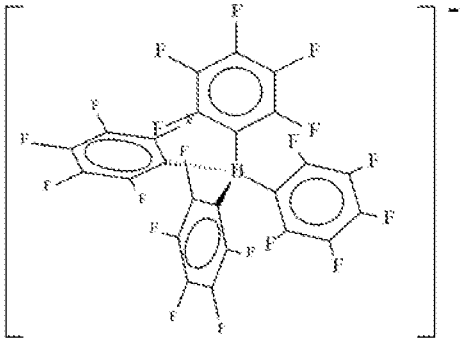
Table 3

		IE1	IE2	IE3
Reactor Configuration	Type	Dual Series	Dual Series	Dual Series
Comonomer type	Type	None	1-octene	1-octene
First Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	5.60	6.05	5.07
First Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.00	0.01	0.005
First Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	3.1E-04	2.8E-04	1.7E-04
First Reactor Temperature	°C	155	156	159

First Reactor Pressure	barg	35	35	34
First Reactor Ethylene Conversion	%	71.5	69.7	87.5
First Reactor Catalyst Type	Type	Cat-1	Cat-1	Cat-1
First Reactor Co-Catalyst 1 Type	Type	CoCatalyst-1	CoCatalyst-1	CoCatalyst-1
First Reactor Co-Catalyst 2 Type	Type	CoCatalyst-2	CoCatalyst-2	CoCatalyst-2
First Reactor Co-Catalyst 1 to Catalyst Molar Ratio (B to Zr ratio)	mol/mol	1.8	1.8	1.8
First Reactor Co-Catalyst 2 to Catalyst Molar Ratio (Al to Zr ratio)	mol/mol	77.0	74.9	37.2
First Reactor Residence Time	min	17.2	17.2	13.2
Percentage of Total Ethylene Feed to First Reactor	wt%	46.9%	51.3%	62.2%
Second Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	2.54	2.58	1.83
Second Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	0.00	0.003	0.0006
Second Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	2.8E-05	2.4E-04	1.3E-03
Second Reactor Temperature	°C	205	205	205
Second Reactor Pressure	barg	35	34	34
Second Reactor Ethylene Conversion	%	91.6	89.7	85.0
Second Reactor Catalyst Type	Type	Cat-2	Cat-2	Cat-2
Second Reactor Co-Catalyst 1 Type	Type	CoCatalyst-1	CoCatalyst-1	CoCatalyst-1
Second Reactor Co-Catalyst 2 Type	Type	CoCatalyst-2	CoCatalyst-2	CoCatalyst-2
Second Reactor Co-Catalyst 1 to Catalyst Molar Ratio (B to Zr ratio)	mol/mol	26.0	24.5	26.5
Second Reactor Co-Catalyst 2 Al Concentration	ppm	0.5	0.5	0.5
Second Reactor Residence Time	min	6.0	6.4	5.5

Table 4



Cat-2	
Co-catalyst 1	R_2MeNH^+ (R = hydrogenated tallow alkyl) 
Co-catalyst 2	modified methyl aluminoxane

In addition, the following compositions are used as comparatives:

- DOW™ DGDA-6098 NT 7 (“CE2”): a polyethylene composition commercially available from The Dow Chemical Company (Midland, Michigan).
- UNIVAL™ DMDA-6400 NT 7 (“CE3”) a polyethylene composition commercially available from The Dow Chemical Company (Midland, Michigan).

The Comparative and Inventive Examples have the following properties as measured in accordance with the test methods above. The first polyethylene component is abbreviated “Comp 1” and second polyethylene component is abbreviated “Comp 2” in the table below.

Table 4 - Properties of Inventive and Comparative Examples

	IE1	IE2	IE3	CE1	CE2	CE3	CE4
Density (g/cc)	0.957	0.957	0.958	0.956	0.958	0.962	0.955
MI (dg/min)	0.78	1.30	1.35	1.30	0.50	0.91	0.85
Mw/Mn	3.18	5.35	5.65	3.64	10.31	9.05	5.67
Mz (kg/mol)	285.3	375.5	266.1	421.3	1613.2	1351.1	286.5
Comp 1 density (g/cm³)	0.943	0.941	0.947	NA	NA	NA	0.946

Comp 2 density (g/cm³)	0.957	0.962	0.969	NA	NA	NA	0.966
Comp 1 Mw (kg/mol)	216.0	254.9	152.7	NA	NA	NA	165.4
Comp 2 Mw (kg/mol)	59.6	38.3	20.4	NA	NA	NA	27.1
Comp 1 weight fraction	0.35	0.35	0.60	NA	NA	NA	0.55
Comp 1 Mw/Mn	2.23	2.23	2.24	NA	NA	NA	2.70
Comp 2 Mw/Mn	2.21	2.44	2.38	NA	NA	NA	2.59

Films are formed from the polyethylene compositions (e.g., IE1 polyethylene composition is formed into film IE1 and so on per Tables 4 and 5). The gloss, total haze, and internal haze are measured. Each film is comprised of 99% of each of the inventive and comparative examples and 1% processing aid master batch commercially available from Ingenia polymers. The films are extruded on a single extruder mono-layer blown film line. The nominal film thickness is 25 microns. The line was comprised of a 3.5 inch, 30 L/D DSBII screw, 8 inch monolayer die, 70 mil die gap and internal bubble cooling (IBC). The melt temperature is 200° C-220° C. The blow-up ratio is 2.5:1. The output rate is 250 lbs/hr.

10 **Table 5 – Gloss and Haze**

	IE1	IE2	IE3	CE1	CE2	CE3	CE4
Gloss	6	6	6	41	17	17	11
Total haze (%)	81	83	86	21	41	52	44
Internal haze (%)	15	17	19	6	7	6	6

IE1-3 have significantly lower gloss. For example, in comparing IE 1 versus CE 1, the compositions have a similar density, Mw/Mn and Mz, but IE1 has significantly lower gloss. The polyethylene compositions characteristics, including the Mw/Mn, Mz and component Mw/Mn, result in films having a matte surface with high haze and low gloss in comparison to comparative examples.

That which is claimed:

1. A polyethylene composition comprising:
 - (a) from 30 to 70 wt.% of a first polyethylene component having a molecular weight distribution (Mw/Mn) of 1.50 to 2.50;
 - 5 (b) from 30 to 70 wt.% of a second polyethylene component having a molecular weight distribution (Mw/Mn) of 1.50 to 2.50;wherein the wt.% of the first polyethylene component and second polyethylene component is based on the total weight of the polyethylene composition, wherein the first polyethylene component has a higher weight average molecular weight than the second polyethylene component, wherein the polyethylene composition has a density of 0.950 to 10 0.960 g/cm³, a melt index (I₂) of 0.5 to 6.0 g/10 min, a molecular weight distribution (Mw/Mn) of 2.0 to 6.0, and a Mz of 100,000 to 500,000 g/mol.
2. The polyethylene composition of claim 1, wherein the second polyethylene 15 component has a density greater than the first polyethylene component.
3. The polyethylene composition of any preceding claim, wherein the molecular weight distribution (Mw/Mn) of the composition is in the range of 3.0 to 5.5.
- 20 4. The polyethylene composition of any preceding claim, wherein the melt index (I₂) of the composition is from 0.5 to 3.0 g/10 min.
5. The polyethylene composition of any preceding claim, wherein the first polyethylene component has a Mw of greater than 80,000 g/mol and a density of less than 0.958 g/cm³. 25
6. The polyethylene composition of any preceding claim, wherein the second polyethylene component has a Mw of less than 80,000 g/mol and a density greater than 0.958 g/cm³.
- 30 7. A film comprising the polyethylene composition of claims 1-6, wherein the film has a gloss of less than 10%.
8. The film of claim 7, wherein the film has a total haze of greater than 60%.

9. The film of claims 7-8, wherein the film has an internal haze of greater than 8%.
10. The film of claims 7-9, wherein the film comprises an outer layer comprising the polyethylene composition of claims 1-6 and an inner layer in adhering contact with the outer layer.
11. The film of claim 10, wherein the inner layer comprises a low density polyethylene.
12. The film of claims 7-11, wherein the film is a blown film.
13. The film of claims 7-12, wherein the film comprises greater than 95 wt.% polyethylene.
14. A label comprising the film of any of the preceding claims 7-13.
15. A package comprising the film of any of claims 7-13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/041215

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08L23/06	C08F210/16
		C08F110/02
		C08F2/00
		C08F4/641
	B32B27/32	
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B32B C08F C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/214584 A1 (NOVA CHEM INT SA [CH]) 28 October 2021 (2021-10-28)	1 - 6
A	the whole document	7 - 15

X	WO 2022/195513 A1 (NOVA CHEM INT SA [CH]) 22 September 2022 (2022-09-22)	1 - 6
A	the whole document	7 - 15

X	WO 2022/195512 A1 (NOVA CHEM INT SA [CH]) 22 September 2022 (2022-09-22)	1 - 6
A	the whole document	7 - 15

X	CA 2 629 576 C (NOVA CHEMICALS CORP [CA]) 5 January 2016 (2016-01-05)	1 - 6
A	the whole document	7 - 15

☐ Further documents are listed in the continuation of Box C.		
☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date		"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means		"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search		Date of mailing of the international search report
7 November 2024		22/11/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Balmer, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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