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(54) Title: BREATHABLE FILMS AND ARTICLES INCORPORATING SAME

(57) Abstract: Breathable films formed from polyethylene are provided that can have desirable properties. In one aspect, a breathable film comprises a layer formed from a composition comprising a first composition, wherein the first composition comprises at least one ethylene-based polymer and wherein the first composition comprises a MWCDI value greater than 0.9, and a melt index ratio (I10/I2) that meets the following equation: $I10/I2 \geq 7.0 - 1.2 \times \log(I2)$.



BREATHABLE FILMS AND ARTICLES INCOPORATING SAME

FIELD

5 The present invention relates generally to breathable films and to articles incorporating breathable films.

INTRODUCTION

Breathable films are widely used in hygiene applications such as diaper backsheets. Persons of skill in the art generally understand breathable films to have a microporous morphology with some ability to allow the passage of moisture vapor. *See, e.g.,* Wu et al., “Novel Microporous Films and Their Composites,” *Journal of Engineered Fibers and Fabrics*, Vol. 2, Issue 1, at 49-59 (2007).

10 Breathable films are typically made by incorporating 40 to 60% of a mineral filler, such as calcium carbonate (CaCO_3), into polyolefin resin, such as polyethylene or polypropylene or combinations of these materials, making a cast or blown film, and stretching or orienting the cast or blown film via machine direction orientation (“MDO”) rolls, via tentering, or via intermeshing gears
15 whereby the film is ringrolled, or incrementally stretched in one or both of the machine direction or cross direction below the melting point of the polyolefin resin. The breathability or water vapor transmission rate (WVTR) of the film is important for some applications, such as diaper backsheet films, protective clothing, surgical suits, and housewrap. In these applications, films can act as a liquid barrier while permitting the transmission of water vapor to provide benefits such as protection
20 and comfort to the end-user in the case of hygiene and medical applications and protection from the elements without the accumulation of moisture in the case of housewrap.

For diaper backsheet applications, breathable films need a good balance of processability, stiffness and toughness. Processability, in terms of draw down capability, is needed during the extrusion and semi-solid state stretching steps of the process to ensure good, uniform draw down
25 without breaks. Stiffness, often measured as film modulus, enables good dimension stability for films as they go through the high speed film printing and diaper making processes. This ultimately provides staple print repeat lengths and predictable web widths. Toughness is needed to prevent film puncture due to the presence of super absorbent polymer (SAP) particles in the absorbent core next to the film and to prevent leakers formed by hydrohead pressure due to a saturated absorbent core
30 and the weight of the end-user.

While ethylene-based polymers have been used for breathable films, there remains a need for ethylene-based compositions that can be used in the manufacture of breathable films having desirable properties and related articles.

SUMMARY

5 The present invention utilizes ethylene-based polymers exhibiting certain features in the formation of breathable films with desirable properties. For example, in some embodiments, the breathable films provide desirable processability, stiffness, toughness, and/or WVTR values for hygiene and other applications.

10 In one aspect, the present invention provides a breathable film comprising a layer formed from a composition comprising a first composition, wherein the first composition comprises at least one ethylene-based polymer and wherein the first composition comprises a MWCDI value greater than 0.9, and a melt index ratio (I10/I2) that meets the following equation: $I10/I2 \geq 7.0 - 1.2 \times \log(I2)$.

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

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the plot of “SCB_f versus IR5 Area Ratio” for ten SCB Standards.

Figure 2 depicts the several GPC profiles for the determination of IR5 Height Ratio for Inventive First Composition 2.

Figure 3 depicts the plot of “SCB_f versus Polyethylene Equivalent molecular Log Mw_i (GPC)” for Inventive First Composition 2.

Figure 4 depicts a plot of the “Mole Percent Comonomer versus Polyethylene Equivalent Log Mw_i (GPC)” for Inventive First Composition 2.

Figure 5 depicts some GPC MWD profiles and corresponding comonomer distribution overlays for some inventive and comparative compositions (density 0.916-0.919 g/cc).

Figure 6 depicts some GPC MWD profiles and corresponding comonomer distribution overlays for some inventive and comparative compositions (density 0.924-0.926 g/cc).

Figure 7 depicts some GPC MWD profiles and corresponding comonomer distribution overlays for some inventive and comparative compositions (Cast stretch).

DETAILED DESCRIPTION

30 It has been discovered that the inventive compositions can be used to form inventive breathable films and related products. Such compositions contain an ethylene-based polymer that

has a superior comonomer distribution, which is significantly higher in comonomer concentration, and a good distribution of comonomer, in the high molecular weight polymer molecules, and is significantly lower in comonomer concentration in the low molecular weight polymer molecules, as compared to conventional polymers of the art at the same overall density. It has also been
5 discovered that the ethylene-based polymer has low LCB (Long Chain Branches), as indicated by low ZSVR, as compared to conventional polymers. As a result of this optimized distribution of the comonomer, as well as the inherent low LCB nature, the inventive compositions have more tie chains, and thus, improved film toughness. The inventive compositions can be useful in forming the inventive breathable films and related products of the present invention.

10 The invention provides a composition comprising a first composition, comprising at least one ethylene-based polymer, wherein the first composition comprises a MWCDI value greater than 0.9, and a melt index ratio (I_{10}/I_2) that meets the following equation: $I_{10}/I_2 \geq 7.0 - 1.2 \times \log(I_2)$.

The inventive composition may comprise a combination of two or more embodiments described herein.

15 The first composition may comprise a combination of two or more embodiments as described herein.

The ethylene-based polymer may comprise a combination of two or more embodiments as described herein.

In one embodiment, the first composition has a MWCDI value less than, or equal to, 10.0,
20 further less than, or equal to, 8.0, further less than, or equal to, 6.0.

In one embodiment, the first composition has a MWCDI value less than, or equal to, 5.0, further less than, or equal to, 4.0, further less than, or equal to, 3.0.

In one embodiment, the first composition has a MWCDI value greater than, or equal to, 1.0, further greater than, or equal to, 1.1, further greater than, or equal to, 1.2.

25 In one embodiment, the first composition has a MWCDI value greater than, or equal to, 1.3, further greater than, or equal to, 1.4, further greater than, or equal to, 1.5.

In one embodiment, the first composition has a melt index ratio I_{10}/I_2 greater than, or equal to, 7.0, further greater than, or equal to, 7.1, further greater than, or equal to, 7.2, further greater than, or equal to, 7.3.

In one embodiment, the first composition has a melt index ratio I10/I2 less than, or equal to, 9.2, further less than, or equal to, 9.0, further less than, or equal to, 8.8, further less than, or equal to, 8.5.

5 In one embodiment, the first composition has a ZSVR value from 1.2 to 3.0, further from 1.2 to 2.5, further 1.2 to 2.0.

In one embodiment, the first composition has a vinyl unsaturation level greater than 10 vinyls per 1,000,000 total carbons. For example, greater than 20 vinyls per 1,000,000 total carbons, or greater than 50 vinyls per 1,000,000 total carbons, or greater than 70 vinyls per 1,000,000 total carbons, or greater than 100 vinyls per 1,000,000 total carbons.

10 In one embodiment, the first composition has a density in the range of 0.910 to 0.940 g/cm³, for example from 0.910 to 0.935 g/cm³, or from 0.910 to 0.930 g/cm³, or from 0.910 to 0.925 g/cm³. For example, the density can be from a lower limit of 0.910, 0.912, or 0.914 g/cm³, to an upper limit of 0.925, 0.927, 0.930, or 0.935 g/cm³ (1 cm³ = 1 cc).

15 In one embodiment, the first composition has a melt index (I₂ or I₂; at 190°C / 2.16kg) from 0.1 to 50 g/10 minutes, for example from 0.1 to 30 g/10 minutes, or from 0.1 to 20 g/10 minutes, or from 0.1 to 10 g/10 minutes. For example, the melt index (I₂ or I₂; at 190°C / 2.16 kg) can be from a lower limit of 0.1, 0.2, or 0.5 g/10 minutes, to an upper limit of 1.0, 2.0, 3.0, 4.0, 5.0, 10, 15, 20, 25, 30, 40, or 50 g/10 minutes.

20 In one embodiment, the first composition has a molecular weight distribution, expressed as the ratio of the weight average molecular weight to number average molecular weight (M_w/M_n ; as determined by conv. GPC) in the range of from 2.2 to 5.0. For example, the molecular weight distribution (M_w/M_n) can be from a lower limit of 2.2, 2.3, 2.4, 2.5, 3.0, 3.2, or 3.4, to an upper limit of 3.9, 4.0, 4.1, 4.2, 4.5, 5.0.

25 In one embodiment, the first composition has a number average molecular weight (M_n ; as determined by conv. GPC) in the range from 10,000 to 50,000 g/mole. For example, the number average molecular weight can be from a lower limit of 10,000, 20,000, or 25,000 g/mole, to an upper limit of 35,000, 40,000, 45,000, or 50,000 g/mole.

In one embodiment, the first composition has a weight average molecular weight (M_w ; as determined by conv. GPC) in the range from 70,000 to 200,000 g/mole. For example, the number

average molecular weight can be from a lower limit of 70,000, 75,000, or 78,000 g/mole, to an upper limit of 120,000, 140,000, 160,000, 180,000 or 200,000 g/mole.

In one embodiment, the first composition has a melt viscosity ratio, $\text{Eta}^*_{0.1} / \text{Eta}^*_{100}$, in the range from 2.2 to 7.0. For example, the number average molecular weight can be from a lower limit
5 of 2.2, 2.3, 2.4 or 2.5, to an upper limit of 6.0, 6.2, 6.5, or 7.0.

In one embodiment, the ethylene-based polymer is an ethylene/ α -olefin interpolpolymer, and further an ethylene/ α -olefin copolymer.

In one embodiment, the first ethylene-based polymer is an ethylene/ α -olefin interpolpolymer, and further an ethylene/ α -olefin copolymer.

10 In one embodiment, the α -olefin has less than, or equal to, 20 carbon atoms. For example, the α -olefin comonomers may preferably have 3 to 10 carbon atoms, and more preferably 3 to 8 carbon atoms. Exemplary α -olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. The one or more α -olefin comonomers may, for example, be selected from the group consisting of propylene,
15 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-butene, 1-hexene and 1-octene, and further 1-hexene and 1-octene.

In one embodiment, the ethylene-based polymer, or first ethylene-based polymer, has a molecular weight distribution (M_w/M_n ; as determined by conv. GPC) in the range from 1.5 to 4.0, for example, from 1.5 to 3.5, or from 2.0 to 3.0. For example, the molecular weight distribution
20 (M_w/M_n) can be from a lower limit of 1.5, 1.7, 2.0, 2.1, or 2.2, to an upper limit of 2.5, 2.6, 2.8, 3.0, 3.5, or 4.0.

In one embodiment, the first composition further comprises a second ethylene-based polymer. In a further embodiment, the second ethylene-based polymer is an ethylene/ α -olefin interpolpolymer, and further an ethylene/ α -olefin copolymer, or a LDPE.

25 In one embodiment, the α -olefin has less than, or equal to, 20 carbon atoms. For example, the α -olefin comonomers may preferably have 3 to 10 carbon atoms, and more preferably 3 to 8 carbon atoms. Exemplary α -olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. The one or more α -olefin comonomers may, for example, be selected from the group consisting of propylene,
30 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-butene, 1-hexene and 1-octene, and further 1-hexene and 1-octene.

In one embodiment, the second ethylene-based polymer is a heterogeneously branched ethylene/ α -olefin interpolmer, and further a heterogeneously branched ethylene/ α -olefin copolymer. Heterogeneously branched ethylene/ α -olefin interpolmers and copolymers are typically produced using Ziegler/Natta type catalyst system, and have more comonomer distributed in the lower
5 molecular weight molecules of the polymer.

In one embodiment, the second ethylene-based polymer has a molecular weight distribution (M_w/M_n) in the range from 3.0 to 5.0, for example from 3.2 to 4.6. For example, the molecular weight distribution (M_w/M_n) can be from a lower limit of 3.2, 3.3, 3.5, 3.7, or 3.9, to an upper limit of 4.6, 4.7, 4.8, 4.9, or 5.0.

10 In one embodiment, the composition comprises from 50 to 80 wt%, or from 50 to 85 wt%, or from 50 to 90 wt%, or from 50 to 95 wt% of the first composition, based on the weight of the composition.

In one embodiment, the composition comprises greater than, or equal to, 80 wt%, or greater than, or equal to, 85 wt%, or greater than, or equal to, 90 wt%, or greater than, or equal to, 95 wt%,
15 or greater than, or equal to 98 wt% of the first composition, based on the weight of the composition.

In one embodiment, the composition further comprises another polymer. In a further embodiment, the polymer is selected from the following: a LLDPE, a VLDPE (a very low density polyethylene), a MDPE, a LDPE, a HDPE, a HMWHDPE (a high molecular weight HDPE), a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer,
20 an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate, a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof.

In one embodiment, the composition further comprises a LDPE. In a further embodiment, the LDPE is present in an amount from 5 to 50 wt%, further from 10 to 40 wt%, further from 15 to
25 30 wt%, based on the weight of the composition. In a further embodiment, the LDPE has a density from 0.915 to 0.930 g/cc, and a melt index (I2) from 0.15 to 30 g/10 min, further from 0.25 to 20 g/10 min.

In one embodiment, the composition further comprises one or more additives.

The invention also provides an article comprising at least one component formed from an
30 inventive composition as described herein. In a further embodiment, the article is a film.

In some embodiments, the present invention relates to a breathable film formed from any of the inventive compositions as described herein. In some embodiments, a first composition (formed from an inventive composition described herein) in the breathable film may have an MWCDI value less than, or equal to 10.0. In some embodiments, the first composition used in the breathable film has a density of 0.910 to 0.950 g/cm³ and/or a melt index (I2) of 0.5 to 30 g/10 minutes. The first composition used in the breathable film, in some embodiments, has a density of 0.915 to 0.940 g/cm³. In some embodiments where the breathable film is a cast film, the melt index can be from 0.8 to 15 g/10 minutes, or from 1.5 to 5 g/10 minutes. In some embodiments where the breathable film is a blown film, the melt index can be from 0.7 to 1.5 g/10 minutes.

In some embodiments, the breathable film further comprises 40 to 65 percent by weight of a mineral filler (e.g., CaCO₃).

A breathable film, in some embodiments, has a basis weight of 10 to 20 g/m², or of 12 to 20 g/m², or of 8 to 18 g/m².

In some embodiments, the breathable film is a monolayer film. The breathable film, in some embodiments, is a multilayer film. In some embodiments, the breathable film comprises up to 7 layers or, in the case of microlayer films, could comprise greater than 15 or 25 layers.

In some embodiments, a first layer of the breathable film can comprise, in addition to an inventive composition, a second polymer, wherein the second polymer is selected from the following: a LLDPE, a VLDPE, a LDPE, a MDPE, a HDPE, a HMWHDPE, a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate, a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof.

In some embodiments where the breathable film is a multilayer film, the film can further comprise a second layer, wherein the second layer comprises a polymer selected from the following: the inventive composition, a LLDPE, a VLDPE (a very low density polyethylene), a MDPE, a LDPE, a HDPE, a HMWHDPE (a high molecular weight HDPE), a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate, an isobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof.

The breathable film, in some embodiments, comprises at least 30 weight percent of any of the inventive compositions disclosed herein. In some embodiments, the breathable film comprises up to 60 weight percent of any of the inventive compositions disclosed herein. The breathable film, in some embodiments, comprises from 40 to 60 weight percent of an inventive composition, or from 5 45 to 55 weight percent of an inventive composition.

In some embodiments, a breathable film exhibits a water vapor transmission rate of at least 100 g/m²-day-atm and up to 10,000 g/m²-day-atm, preferably from 500 g/m²-day-atm to 10,000 g/m²-day-atm, or from 1,000 to 6,000 g/m²-day-atm, or from 1,500 to 6,000 g/m²-day-atm.

10 The breathable film, in some embodiments, exhibits a hydrohead of at least 60 cm as measured by EN 20811.

In some embodiments, the breathable film is oriented in at least the machine direction.

Some embodiments of the present invention relate to laminates comprising a breathable film as disclosed herein. In some such embodiments, the laminate may further comprise a non-woven material. Some embodiments of the present invention relate to an article comprising a laminate as 15 disclosed herein.

Some embodiments of the present invention relate to an article comprising a breathable film as disclosed herein. Non-limiting examples of such articles can include backsheets for baby diapers, training pants, adult incontinence products, breathable barrier surgical gowns, housewrap, and filtration products.

20 **Polymerization**

Polymerization processes include, but are not limited to, solution polymerization processes, using one or more conventional reactors, e.g., loop reactors, isothermal reactors, adiabatic reactors, stirred tank reactors, autoclave reactors in parallel, series, and/or any combinations thereof. The ethylene based polymer compositions may, for example, be produced via solution phase 25 polymerization processes, using one or more loop reactors, adiabatic reactors, and combinations thereof.

In general, the solution phase polymerization process occurs in one or more well mixed reactors, such as one or more loop reactors and/or one or more adiabatic reactors at a temperature in the range from 115 to 250°C; for example, from 135 to 200°C, and at pressures in the range of from 30 300 to 1000 psig, for example, from 450 to 750 psig.

In one embodiment, the ethylene based polymer composition (e.g., the first composition of claim 1) may be produced in two loop reactors in series configuration, the first reactor temperature is in the range from 115 to 200°C, for example, from 135 to 165°C, and the second reactor temperature is in the range from 150 to 210°C, for example, from 185 to 200°C. In another embodiment, the ethylene based polymer composition may be produced in a single reactor, and the reactor temperature is in the range from 115 to 200°C, for example from 130 to 190°C. The residence time in a solution phase polymerization process is typically in the range from 2 to 40 minutes, for example from 5 to 20 minutes. Ethylene, solvent, one or more catalyst systems, optionally one or more cocatalysts, and optionally one or more comonomers, are fed continuously to one or more reactors. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E from ExxonMobil Chemical. The resultant mixture of the ethylene based polymer composition and solvent is then removed from the reactor or reactors, and the ethylene based polymer composition is isolated. Solvent is typically recovered via a solvent recovery unit, i.e., heat exchangers and separator vessel, and the solvent is then recycled back into the polymerization system.

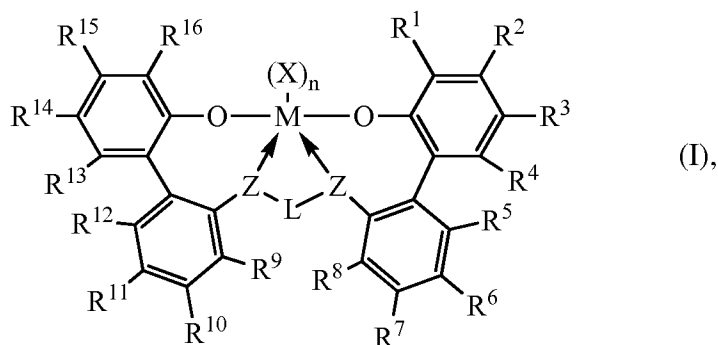
In one embodiment, the ethylene based polymer composition may be produced, via a solution polymerization process, in a dual reactor system, for example a dual loop reactor system, wherein ethylene, and optionally one or more α -olefins, are polymerized in the presence of one or more catalyst systems, in one reactor, to produce a first ethylene-based polymer, and ethylene, and optionally one or more α -olefins, are polymerized in the presence of one or more catalyst systems, in a second reactor, to produce a second ethylene-based polymer. Additionally, one or more cocatalysts may be present.

In another embodiment, the ethylene based polymer composition may be produced via a solution polymerization process, in a single reactor system, for example, a single loop reactor system, wherein ethylene, and optionally one or more α -olefins, are polymerized in the presence of one or more catalyst systems. Additionally, one or more cocatalysts may be present.

As discussed above, the invention provides a process to form a composition comprising at least two ethylene-based polymers, said process comprising the following:

polymerizing ethylene, and optionally at least one comonomer, in solution, in the presence of a catalyst system comprising a metal-ligand complex of Structure I, to form a first ethylene-based polymer; and

polymerizing ethylene, and optionally at least one comonomer, in the presence of a catalyst system comprising a Ziegler/Natta catalyst, to form a second ethylene-based polymer; and wherein Structure I is as follows:



5 wherein:

M is titanium, zirconium, or hafnium, each, independently, being in a formal oxidation state of +2, +3, or +4; and

n is an integer from 0 to 3, and wherein when n is 0, X is absent; and

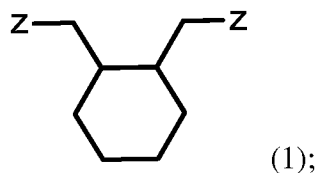
each X, independently, is a monodentate ligand that is neutral, monoanionic, or dianionic; or

10 two Xs are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; and

X and n are chosen, in such a way, that the metal-ligand complex of formula (I) is, overall, neutral; and

each Z, independently, is O, S, N(C₁-C₄₀)hydrocarbyl, or P(C₁-C₄₀)hydrocarbyl; and

wherein the Z-L-Z fragment is comprised of formula (1):



15

R¹ through R¹⁶ are each, independently, selected from the group consisting of the following: a substituted or unsubstituted (C₁-C₄₀)hydrocarbyl, a substituted or unsubstituted

(C₁-C₄₀)heterohydrocarbyl, Si(R^C)₃, Ge(R^C)₃, P(R^P)₂, N(R^N)₂, OR^C, SR^C, NO₂, CN, CF₃,

R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R)-, (R^C)₂NC(O)-, halogen atom,

20 hydrogen atom; and wherein each R^C is independently a (C₁-C₃₀)hydrocarbyl; R^P is a

(C₁-C₃₀)hydrocarbyl; and R^N is a (C₁-C₃₀)hydrocarbyl; and

wherein, optionally, two or more R groups (from R¹ through R¹⁶) can combine together into one or more ring structures, with such ring structures each, independently, having from 3 to 50 atoms in the ring, excluding any hydrogen atom.

5 An inventive process may comprise a combination of two or more embodiments as described herein.

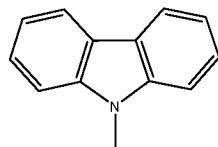
In one embodiment, said process comprises polymerizing ethylene, and optionally at least one α -olefin, in solution, in the presence of a catalyst system comprising a metal-ligand complex of Structure I, to form a first ethylene-based polymer; and polymerizing ethylene, and optionally at least one α -olefin, in the presence of a catalyst system comprising a Ziegler/Natta catalyst, to form a
10 second ethylene-based polymer. In a further embodiment, each α -olefin is independently a C1-C8 α -olefin.

In one embodiment, optionally, two or more R groups from R⁹ through R¹³, or R⁴ through R⁸ can combine together into one or more ring structures, with such ring structures each, independently, having from 3 to 50 atoms in the ring, excluding any hydrogen atom.

15 In one embodiment, M is hafnium.

In one embodiment, R³ and R¹⁴ are each independently an alkyl, and further a C1-C3 alkyl, and further methyl.

In one embodiment, R¹ and R¹⁶ are each as follows:

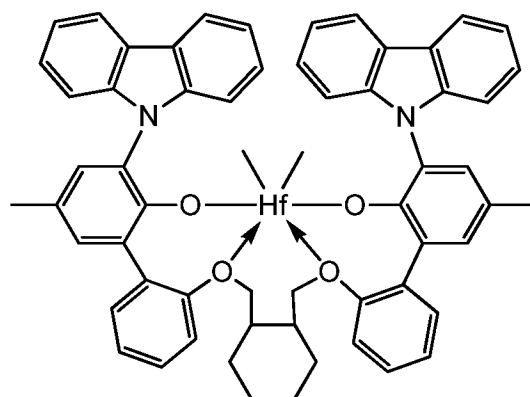


20 In one embodiment, each of the aryl, heteroaryl, hydrocarbyl, heterohydrocarbyl, Si(R^C)₃, Ge(R^C)₃, P(R^P)₂, N(R^N)₂, OR^C, SR^C, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R)-, (R^C)₂NC(O)-, hydrocarbylene, and heterohydrocarbylene groups, independently, is unsubstituted or substituted with one or more R^S substituents; and each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C₁-C₁₈)alkyl, F₃C-,
25 FCH₂O-, F₂HCO-, F₃CO-, R₃Si-, R₃Ge-, RO-, RS-, RS(O)-, RS(O)₂-, R₂P-, R₂N-, R₂C=N-, NC-, RC(O)O-, ROC(O)-, RC(O)N(R)-, or R₂NC(O)-, or two of the R^S are taken together to form

an unsubstituted (C₁-C₁₈)alkylene, wherein each R independently is an unsubstituted (C₁-C₁₈)alkyl.

In one embodiment, two or more of R¹ through R¹⁶ do not combine to form one or more ring structures.

- 5 In one embodiment, the catalyst system suitable for producing the first ethylene/ α -olefin interpolpolymer is a catalyst system comprising bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxyethyl)-methylene-1,2-cyclohexanediylhafnium (IV) dimethyl, represented by the following Structure IA:



(IA).

- 10 The Ziegler/Natta catalysts suitable for use in the invention are typical supported, Ziegler-type catalysts, which are particularly useful at the high polymerization temperatures of the solution process. Examples of such compositions are those derived from organomagnesium compounds, alkyl halides or aluminum halides or hydrogen chloride, and a transition metal compound. Examples of such catalysts are described in U.S. Pat Nos. 4,612,300; 4,314,912; and 4,547,475; the teachings
15 of which are incorporated herein by reference.

- Particularly suitable organomagnesium compounds include, for example, hydrocarbon soluble dihydrocarbylmagnesium, such as the magnesium dialkyls and the magnesium diaryls. Exemplary suitable magnesium dialkyls include, particularly, n-butyl-sec-butylmagnesium, diisopropylmagnesium, di-n-hexylmagnesium, isopropyl-n-butyl-magnesium, ethyl-n-hexyl-
20 magnesium, ethyl-n-butylmagnesium, di-n-octylmagnesium, and others, wherein the alkyl has from 1 to 20 carbon atoms. Exemplary suitable magnesium diaryls include diphenylmagnesium, dibenzylmagnesium and ditolylmagnesium. Suitable organomagnesium compounds include alkyl and aryl magnesium alkoxides and aryloxides and aryl and alkyl magnesium halides, with the halogen-free organomagnesium compounds being more desirable.

Halide sources include active non-metallic halides, metallic halides, and hydrogen chloride. Suitable non-metallic halides are represented by the formula $R'X$, wherein R' is hydrogen or an active monovalent organic radical, and X is a halogen. Particularly suitable non-metallic halides include, for example, hydrogen halides and active organic halides, such as *t*-alkyl halides, allyl halides, benzyl halides and other active hydrocarbyl halides. By an active organic halide is meant a hydrocarbyl halide that contains a labile halogen at least as active, i.e., as easily lost to another compound, as the halogen of *sec*-butyl chloride, preferably as active as *t*-butyl chloride. In addition to the organic monohalides, it is understood that organic dihalides, trihalides and other polyhalides that are active, as defined hereinbefore, are also suitably employed. Examples of preferred active non-metallic halides, include hydrogen chloride, hydrogen bromide, *t*-butyl chloride, *t*-amyl bromide, allyl chloride, benzyl chloride, crotyl chloride, methylvinyl carbinyl chloride, *a*-phenylethyl bromide, diphenyl methyl chloride, and the like. Most preferred are hydrogen chloride, *t*-butyl chloride, allyl chloride and benzyl chloride.

Suitable metallic halides include those represented by the formula $MR_y-a X_a$, wherein: M is a metal of Groups IIB, IIIA or IVA of Mendeleev's periodic Table of Elements; R is a monovalent organic radical; X is a halogen; y has a value corresponding to the valence of M ; and " a " has a value from 1 to y . Preferred metallic halides are aluminum halides of the formula $AlR_{3-a} X_a$, wherein each R is independently hydrocarbyl, such as alkyl; X is a halogen; and " a " is a number from 1 to 3. Most preferred are alkylaluminum halides, such as ethylaluminum sesquichloride, diethylaluminum chloride, ethylaluminum dichloride, and diethylaluminum bromide, with ethylaluminum dichloride being especially preferred. Alternatively, a metal halide, such as aluminum trichloride, or a combination of aluminum trichloride with an alkyl aluminum halide, or a trialkyl aluminum compound may be suitably employed.

Any of the conventional Ziegler-Natta transition metal compounds can be usefully employed, as the transition metal component in preparing the supported catalyst component. Typically, the transition metal component is a compound of a Group IVB, VB, or VIB metal. The transition metal component is generally, represented by the formulas: $TrX'_{4-q} (OR)_q$, $TrX'_{4-q} (R_2)_q$, VOX'_3 and $VO(OR)_3$.

Tr is a Group IVB, VB, or VIB metal, preferably a Group IVB or VB metal, preferably titanium, vanadium or zirconium; q is 0 or a number equal to, or less than, 4; X' is a halogen, and R_1

is an alkyl group, aryl group or cycloalkyl group having from 1 to 20 carbon atoms; and R2 is an alkyl group, aryl group, aralkyl group, substituted aralkyls, and the like.

The aryl, aralkyls and substituted aralkyls contain 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms. When the transition metal compound contains a hydrocarbyl group, R2, being an alkyl, cycloalkyl, aryl, or aralkyl group, the hydrocarbyl group will preferably not contain an H atom in the position beta to the metal carbon bond. Illustrative, but non-limiting, examples of aralkyl groups are methyl, neopentyl, 2,2-dimethylbutyl, 2,2-dimethylhexyl; aryl groups such as benzyl; cycloalkyl groups such as 1-norbornyl. Mixtures of these transition metal compounds can be employed if desired.

Illustrative examples of the transition metal compounds include TiCl_4 , TiBr_4 , $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$, $\text{Ti}(\text{OC}_8\text{H}_{17})_2\text{Br}_2$, and $\text{Ti}(\text{OC}_{12}\text{H}_{25})\text{Cl}_3$, $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$, and $\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$. Illustrative examples of vanadium compounds include VCl_4 , VOCl_3 , $\text{VO}(\text{OC}_2\text{H}_5)_3$, and $\text{VO}(\text{OC}_4\text{H}_9)_3$. Illustrative examples of zirconium compounds include ZrCl_4 , $\text{ZrCl}_3(\text{OC}_2\text{H}_5)$, $\text{ZrCl}_2(\text{OC}_2\text{H}_5)_2$, $\text{ZrCl}(\text{OC}_2\text{H}_5)_3$, $\text{Zr}(\text{OC}_2\text{H}_5)_4$, $\text{ZrCl}_3(\text{OC}_4\text{H}_9)$, $\text{ZrCl}_2(\text{OC}_4\text{H}_9)_2$, and $\text{ZrCl}(\text{OC}_4\text{H}_9)_3$.

An inorganic oxide support may be used in the preparation of the catalyst, and the support may be any particulate oxide, or mixed oxide which has been thermally or chemically dehydrated, such that it is substantially free of adsorbed moisture. See U. S. Pat Nos. 4,612,300; 4,314,912; and 4,547,475; the teachings of which are incorporated herein by reference.

In one embodiment, the composition comprises a MWCDI value greater than 0.9.

In one embodiment, the composition comprises a melt index ratio (I_{10}/I_2) that meets the following equation: $I_{10}/I_2 \geq 7.0 - 1.2 \times \log(I_2)$.

The composition may comprise one embodiment, or a combination of two or more embodiments, as listed above for the "first composition."

An inventive process may comprise a combination of two or more embodiments described herein.

Co-catalyst Component

The above described catalyst systems can be rendered catalytically active by contacting it to, or combining it with, the activating co-catalyst, or by using an activating technique, such as those known in the art, for use with metal-based olefin polymerization reactions. Suitable activating co-catalysts, for use herein, include alkyl aluminums; polymeric or oligomeric alumoxanes (also known

as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Aluminoxanes and their preparations are known at, for example, U. S. Patent 6,103,657. Examples of preferred polymeric or oligomeric alumoxanes are methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

Exemplary Lewis acid activating co-catalysts are Group 13 metal compounds containing from 1 to 3 hydrocarbyl substituents as described herein. In some embodiments, exemplary Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum or tri(hydrocarbyl)-boron compounds. In some other embodiments, exemplary Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum or tri(hydrocarbyl)-boron compounds are tri((C₁-C₁₀)alkyl)aluminum or tri((C₆-C₁₈)aryl)boron compounds and halogenated (including perhalogenated) derivatives thereof. In some other embodiments, exemplary Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, in other embodiments, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tri((C₁-C₂₀)hydrocarbyl) borate (e.g., trityl tetrafluoroborate) or a tri((C₁-C₂₀)hydrocarbyl)ammonium tetra((C₁-C₂₀)hydrocarbyl)borane (e.g., bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁-C₂₀)hydrocarbyl)₄N⁺, a ((C₁-C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁-C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁-C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁-C₂₀)hydrocarbyl may be the same or different.

Exemplary combinations of neutral Lewis acid activating co-catalysts include mixtures comprising a combination of a tri((C₁-C₄)alkyl)aluminum and a halogenated tri((C₆-C₁₈)aryl)boron compound, especially a tris(pentafluorophenyl)borane. Other exemplary embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Exemplary embodiments ratios of numbers of moles of

(metal-ligand complex):(tris(pentafluoro-phenylborane): (alumoxane) [e.g., (Group 4 metal-ligand complex):(tris(pentafluoro-phenylborane):(alumoxane)] are from 1:1:1 to 1:10:30, other exemplary embodiments are from 1:1:1.5 to 1:5:10.

Many activating co-catalysts and activating techniques have been previously taught, with
5 respect to different metal-ligand complexes, in the following U.S. patents: US 5,064,802;
US 5,153,157; US 5,296,433; US 5,321,106; US 5,350,723; US 5,425,872; US 5,625,087;
US 5,721,185; US 5,783,512; US 5,883,204; US 5,919,983; US 6,696,379; and US 7,163,907.
Examples of suitable hydrocarbyloxides are disclosed in US 5,296,433. Examples of suitable
Bronsted acid salts for addition polymerization catalysts are disclosed in US 5,064,802;
10 US 5,919,983; US 5,783,512. Examples of suitable salts of a cationic oxidizing agent and a non-
coordinating, compatible anion, as activating co-catalysts for addition polymerization catalysts, are
disclosed in US 5,321,106. Examples of suitable carbenium salts as activating co-catalysts for
addition polymerization catalysts are disclosed in US 5,350,723. Examples of suitable silylium salts,
as activating co-catalysts for addition polymerization catalysts, are disclosed in US 5,625,087.
15 Examples of suitable complexes of alcohols, mercaptans, silanols, and oximes with
tris(pentafluorophenyl)borane are disclosed in US 5,296,433. Some of these catalysts are also
described in a portion of US 6,515,155 B1, beginning at column 50, at line 39, and going through
column 56, at line 55, only the portion of which is incorporated by reference herein.

In some embodiments, the above described catalyst systems can be activated to form an
20 active catalyst composition by combination with one or more cocatalyst, such as a cation forming
cocatalyst, a strong Lewis acid, or a combination thereof. Suitable cocatalysts for use include
polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible,
noncoordinating, ion forming compounds. Exemplary suitable cocatalysts include, but are not
limited to, modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl,
25 tetrakis(pentafluorophenyl)borate(1-) amine, triethyl aluminum (TEA), and any combinations
thereof.

In some embodiments, one or more of the foregoing activating co-catalysts are used in
combination with each other. In one embodiment, a combination of a mixture of a
tri((C₁-C₄)hydrocarbyl)aluminum, tri((C₁-C₄)hydrocarbyl)borane, or an ammonium borate with an
30 oligomeric or polymeric alumoxane compound, can be used.

Additives, Additional Polymers and Applications

An inventive composition may comprise one or more additives. Additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, fillers (for example, TiO_2 or CaCO_3), opacifiers, nucleators, processing aids, pigments, primary anti-oxidants, secondary anti-oxidants, UV stabilizers, anti-blocks, slip agents, tackifiers, fire retardants, anti-microbial agents, odor reducer agents, anti-fungal agents, and combinations thereof. In some embodiments, an inventive composition may comprise from about 0.001 to about 10 percent by the combined weight of such additives, based on the weight of the composition including such additives.

In breathable film applications (e.g., diaper, training pants, and adult incontinence backsheet films, surgical gowns, protective clothing, housewrap, etc.), large amounts of CaCO_3 , or other mineral fillers, may be incorporated as a filler to increase WVTR and other properties related to breathability. For example, in some embodiments, a breathable film can comprise at least 20% by weight CaCO_3 , or at least 30% by weight CaCO_3 , or at least 40% by weight CaCO_3 based on the total weight of the film. In some embodiments, a breathable film can comprise up to 70% by weight CaCO_3 , or up to 65 % by weight CaCO_3 , or up to 60% by weight CaCO_3 based on the total weight of the film. A breathable film, in some embodiments can comprise from 20% to 70% by weight CaCO_3 , or from 30% to 70% by weight CaCO_3 , or from 40% to 65% by weight CaCO_3 , or from 40% to 60% by weight CaCO_3 based on the total weight of the film.

An inventive composition may further comprise one or more other polymers. For example one or more other ethylene-based polymers (such polymers differ in one or more properties from the ethylene-based polymer of the first composition and the second ethylene-based polymer; i.e., density, melt index, comonomer, M_n , M_w , and/or MWD), or one or more propylene-based polymers, or combinations thereof.

Inventive compositions can be blended with other polymers to provide a resin in some embodiments. Non-limiting examples of other polymers that can be blended with one or more inventive compositions include a LLDPE, a VLDPE, a LDPE, a MDPE, a HDPE, a HMWHDPE, a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate, a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof. Such compositions may be blended via any method, known to a person of ordinary skill in the art,

including, but not limited to, dry blending, and melt blending via any suitable equipment, for example, an extruder. The resin further comprises a mineral filler, such as CaCO_3 , to enable the microporous morphology and breathability that results from stretching the film comprising the resin. As noted in “The Role of Calcium Carbonate in Microporous Film Applications” by Deebea Ansara, Allison Calhoun, and Paul Merriman, PMA124PL, November 2001: “[Typically] stearic acid coated CaCO_3 is used to enable free-flowing CaCO_3 , that is easier to handle, compound, and disperse in the polymer. This coating results in a hydrophobic particle. The orientation process creates microvoids where the polymer separates from the calcium carbonate particles.” Thus, in some embodiments using CaCO_3 as a mineral filler, the CaCO_3 can be coated with stearic acid. In some embodiments, the resin may comprise 45-80% CaCO_3 by weight based on the weight of the compound. In some such embodiments, the resin can provide a good dispersion of the CaCO_3 and can then be let down with other resins to provide a breathable film having a desired CaCO_3 concentration (e.g., 45-60% by weight CaCO_3).

In some embodiments, the present invention relates to a breathable film formed from any of the inventive compositions as described herein. In some embodiments, the breathable film is a monolayer film. The breathable film, in some embodiments, is a multilayer film. Breathable films can be formed from inventive compositions using methods and equipment well-known to those of skill in the art. For example, breathable films can be produced via a blown or cast film extrusion process and then stretched / oriented in a semi-solid state below the melting point of the polymer or polymer blend.

The amount of the inventive composition to use in breathable films of the present invention can depend on a number of factors including, for example, whether the film is a monolayer or multilayer film, the other layers in the film if it is a multilayer film, the desired properties of the film, the end use application of the film, the desired properties of the film, the equipment available to manufacture the film, and others. A breathable film of the present invention, in some embodiments, comprises at least 20 percent by weight of the inventive composition, or at least 30 percent by weight of the inventive composition, or at least 40 percent by weight of the inventive composition.

In embodiments where the breathable film comprises a multilayer film, the number of layers in the film can depend on a number of factors including, for example, the desired properties of the film, the desired thickness of the film, the content of the other layers of the film, whether any of the layers in the film are to be foamed, the end use application of the film, the equipment available to

manufacture the film, and others. A multilayer breathable film can comprise up to 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11 layers in various embodiments.

The inventive composition, in some embodiments, can be used in more than one layer of the film. Other layers within a multilayer film of the present invention can comprise, in various
5 embodiments, a polymer selected from the following: the inventive composition, a LLDPE, a VLDPE (a very low density polyethylene), a MDPE, a LDPE, a HDPE, a HMWHDPE (a high molecular weight HDPE), a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate,
10 an isobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof. In some embodiments, a multilayer film of the present invention can comprise one or more tie layers known to those of skill in the art.

Breathable films can be coextrusions comprising two or more layers in some embodiments. Common film structures include, for example, a/b/a structures, a/b/c structures and others.
15 Individual layers within a film structure can be 1% to 99% of the multilayer film based on the total weight of the film. Exemplary configurations include 10%/80%/10%, 20%/60%/20%, 1%/98%/1%, and others. Breathable films that are coextruded can be advantageous in some applications as they can, in some embodiments, achieve better bonding (e.g. thermal, adhesive, or ultrasonic) between the breathable film and another substrate, impart stiffness, and/or provide different haptics. In such
20 multi-layer films, one or more of the additional layers (in addition to the layer comprising an inventive composition) can comprise a polymer selected from the following: an inventive composition, a LLDPE, a VLDPE, a LDPE, a MDPE, a HDPE, a HMWHDPE, a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an
25 ethylene ethyl acrylate, an ethylene butyl acrylate, a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or combinations thereof.

As noted above, after formation of the film (e.g., via blown or cast film extrusion processes), the film is then stretched or oriented. Often, the film is heated prior to the stretching step to a temperature above its glass transition temperature, but below its melt temperature, such that it is
30 stretched in a semi-solid state. Stretch methods include orientation in the machine direction or the use of ring rolling or intermeshing gears. In machine direction orientation (MDO), the film can then

be heated via contact with heated rollers prior to being stretched between sets of rollers as is known to those of skill in the art. *See, e.g.,* P.C. Wu et al., “Novel Microporous Films and Their Composites,” *Journal of Engineered Fibers and Fabrics*, Vol. 2, Issue 1, 49-59 (2007). The film is typically stretched between driven rollers whereby pairs of consecutive rollers are driven at progressively higher speeds to induce stretching (*see, e.g.,* Wu et al., p. 53 at FIGURE 7). Films are typically stretched from 1.5 to 5x their original length depending upon the properties desired. Higher levels of stretch impart larger pore sizes and higher levels of breathability in the film. Higher stretch can also impart splittiness or low tear properties in the film. Processability or stretch window is measured in terms of the minimum amount of stretch needed to create a uniformly stretched film without the haze variations, often referred to as tiger striping, to the maximum amount of stretch that a film can withstand without creating pinholes or breaks in the web. Films with a larger stretch window can enable a wider range of performance properties and can be more resistant to pinholing and web breaks.

In orientation by ring rolling or with intermeshing gears (IMG), the film may also be heated to a temperature below its melting point via contact with heated rolls. The film is stretched between intermeshing rings or gears. The degree of stretching is controlled by the depth of engagement of an individual ring gear or ring relative to the adjacent ring(s) or gear(s). Such techniques are generally known to those of skill in the art. For example, U.S. Patents 4,116,892 and 4,153,751, which are incorporated herein by reference, provide additional information about ring rolling processes.

In both MDO and IMG processes, the films can be annealed after the stretching process. In some embodiments, the films can be stretched in 1 direction, such as with MDO or a single IMG step, of either machine direction stretching or cross direction stretching. Films can be stretched in two directions in series such as MDO followed by an IMG step to stretch in the cross direction. Another alternative is stretching in the machine direction via IMG followed by cross direction stretching via IMG. Yet another means of multi-direction stretching is via a tentering process.

Breathable films can have basis weights ranging from 8 to 24 grams per square meter or in the alternative, from 10 to 20 g/m² or in the alternative, from 12-18 g/m². The basis weight of the breathable film can depend on a number of factors including the desired properties of the film, the end use application of the film, the equipment available to manufacture the film, the cost allowed by the application, and other factors.

In some embodiments, a breathable film of the present invention can exhibit a water vapor transmission rate of at least $100 \text{ g/m}^2\text{-day-atm}$ when measured in accordance with ASTM D-6701. A breathable film of the present invention, in some embodiments, can exhibit a water vapor transmission rate of at least $100 \text{ g/m}^2\text{-day-atm}$ and up to $10,000 \text{ g/m}^2\text{-day-atm}$ when measured in accordance with ASTM D-6701. In some embodiments, a breathable film of the present invention can exhibit a water vapor transmission rate of at least $500 \text{ g/m}^2\text{-day-atm}$ and up to $10,000 \text{ g/m}^2\text{-day-atm}$ when measured in accordance with ASTM D-6701. A breathable film of the present invention, in some embodiments, can exhibit a water vapor transmission rate of at least $1,000 \text{ g/m}^2\text{-day-atm}$ and up to $6,000 \text{ g/m}^2\text{-day-atm}$ when measured in accordance with ASTM D-6701. A breathable film of the present invention, in some embodiments, can exhibit a water vapor transmission rate of at least $1,500 \text{ g/m}^2\text{-day-atm}$ and up to $6,000 \text{ g/m}^2\text{-day-atm}$ when measured in accordance with ASTM D-6701.

In some embodiments, a breathable film of the present invention can exhibit a hydrohead of at least 60 cm as measured by EN 20811.

It is also contemplated that a breathable film may comprise additional layers, either coextruded, or as a laminate. These layers may be selected to provide additional functionality, for example, layers to provide extra strength, adhesion to another substrate such as a non-woven, and/or aesthetic properties such as feel or appearance.

Some embodiments of the present invention relate to laminates comprising one or more breathable films of the present invention. For example, breathable films of the present invention can be used in film/non-woven laminates. Typical non-wovens for use in such laminates can be spunlaid, airlaid, carded webs, or composites thereof. Typical non-woven composites for use in laminates with a breathable film of the present invention include three beams of spunbond, (e.g., S/S/S), a spunbond / meltblown / spunbond composite (e.g., S/M/S), and others. Common methods for joining the film to the non-wovens include, for example, bonded hot melt adhesive lamination, ultra-sonic bonding, and thermal bonding through a calendar or nip roll.

The present invention also relates to articles comprising at least one component formed from an inventive composition. The component can be, for example, a breathable film or film laminate. Such components can be used in disposable hygiene and medical products as liquid impermeable but breathable layers. Examples of articles comprising such breathable films or film laminates include diapers, training pants, feminine hygiene products, adult incontinence products, medical drapes,

medical gowns, surgical suits, and others. In articles such as diaper, training pants, feminine hygiene products, and adult incontinence products, a breathable film or film laminate is also often referred to as a backsheet. In medical products, a breathable film or film laminate are often referred to as the “barrier layer” as the breathable film or film laminate can prevent contamination from a health care worker to a patient and vice versa. Breathable films can be incorporated into such articles using techniques known to those of skill in the art based on the teachings herein.

DEFINITIONS

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

The term “composition,” as used herein, includes material(s) which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

The term “comprising,” and derivatives thereof, is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein 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 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 (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 interpolymer as defined hereinafter. Trace amounts of impurities may be incorporated into and/or within the polymer.

The term “interpolymer,” as used herein, refers to a polymer 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 term, “olefin-based polymer,” as used herein, refers 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 at least one polymerized comonomer.

5 The term, “ethylene-based polymer,” as used herein, refers to a polymer that comprises a majority amount of polymerized ethylene monomer (based on the total weight of the polymer), and optionally may comprise at least one polymerized comonomer.

The term, “ethylene/ α -olefin interpolymers,” as used herein, refers to an interpolymers that comprises, in polymerized form, a majority amount of ethylene monomer (based on the weight of the interpolymers), and at least one α -olefin.

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

The term “propylene-based polymer,” as used herein, refers to a polymer that comprises, in polymerized form, a majority amount of propylene monomer (based on the total weight of the polymer) and optionally may comprise at least one polymerized comonomer.

TEST METHODS

Melt index

Melt indices I_2 (or $I2$) and I_{10} (or $I10$) were measured in accordance to ASTM D-1238 (method B) at 190°C and at 2.16 kg and 10 kg load, respectively. Their values are reported in g/10 min.

Density

Samples for density measurement were prepared according to ASTM D4703. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

Dynamic Shear Rheology

25 Each sample was compression-molded into “3 mm thick x 25 mm diameter” circular plaque, at 177°C, for five minutes, under 10 MPa pressure, in air. The sample was then taken out of the press and placed on a counter top to cool.

Constant temperature, frequency sweep measurements were performed on an ARES strain controlled rheometer (TA Instruments), equipped with 25 mm parallel plates, under a nitrogen purge. For each measurement, the rheometer was thermally equilibrated, for at least 30 minutes, prior to zeroing the gap. The sample disk was placed on the plate, and allowed to melt for five minutes at

190°C. The plates were then closed to 2 mm, the sample trimmed, and then the test was started. The method had an additional five minute delay built in, to allow for temperature equilibrium. The experiments were performed at 190°C, over a frequency range from 0.1 to 100 rad/s, at five points per decade interval. The strain amplitude was constant at 10%. The stress response was analyzed in terms of amplitude and phase, from which the storage modulus (G'), loss modulus (G''), complex modulus (G^*), dynamic viscosity (η^* or Eta^*), and $\tan \delta$ (or $\tan \delta$) were calculated.

Conventional Gel Permeation Chromatography (conv. GPC)

A GPC-IR high temperature chromatographic system from PolymerChar (Valencia, Spain), was equipped with a Precision Detectors (Amherst, MA), 2-angle laser light scattering detector Model 2040, an IR5 infra-red detector and a 4-capillary viscometer, both from PolymerChar. Data collection was performed using PolymerChar Instrument Control software and data collection interface. The system was equipped with an on-line, solvent degas device and pumping system from Agilent Technologies (Santa Clara, CA).

Injection temperature was controlled at 150 degrees Celsius. The columns used, were three, 10-micron "Mixed-B" columns from Polymer Laboratories (Shropshire, UK). The solvent used was 1,2,4-trichlorobenzene. The samples were prepared at a concentration of "0.1 grams of polymer in 50 milliliters of solvent." The chromatographic solvent and the sample preparation solvent each contained "200 ppm of butylated hydroxytoluene (BHT)." Both solvent sources were nitrogen sparged. Ethylene-based polymer samples were stirred gently at 160 degrees Celsius for three hours. The injection volume was "200 microliters," and the flow rate was "1 milliliters/minute." The GPC column set was calibrated by running 21 "narrow molecular weight distribution" polystyrene standards. The molecular weight (MW) of the standards ranges from 580 to 8,400,000 g/mole, and the standards were contained in six "cocktail" mixtures. Each standard mixture had at least a decade of separation between individual molecular weights. The standard mixtures were purchased from Polymer Laboratories. The polystyrene standards were prepared at "0.025 g in 50 mL of solvent" for molecular weights equal to, or greater than, 1,000,000 g/mole, and at "0.050 g in 50 mL of solvent" for molecular weights less than 1,000,000 g/mole.

The polystyrene standards were dissolved at 80°C, with gentle agitation, for 30 minutes. The narrow standards mixtures were run first, and in order of decreasing "highest molecular weight component," to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene molecular weight using Equation 1 (as described in Williams and

Ward, *J. Polym. Sci., Polym. Letters*, 6, 621 (1968));

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (\text{Eqn. 1}),$$

where M is the molecular weight, A is equal to 0.4316 and B is equal to 1.0.

Number-average molecular weight ($M_n(\text{conv gpc})$), weight average molecular weight ($M_w(\text{conv gpc})$), and z-average molecular weight ($M_z(\text{conv gpc})$) were calculated according to Equations 2-4 below.

$$M_n(\text{conv gpc}) = \frac{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (IR_{\text{measurement channel } i})}{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} \left(IR_{\text{measurement channel } i} / M_{PEi} \right)} \quad (\text{Eqn. 2})$$

$$M_w(\text{conv gpc}) = \frac{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (M_{PEi} IR_{\text{measurement channel } i})}{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (IR_{\text{measurement channel } i})} \quad (\text{Eqn. 3})$$

$$M_z(\text{conv gpc}) = \frac{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (M_{PEi}^2 IR_{\text{measurement channel } i})}{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (M_{PEi} IR_{\text{measurement channel } i})} \quad (\text{Eqn. 4})$$

In Equations 2-4, the RV is column retention volume (linearly-spaced), collected at “1 point per second,” the IR is the baseline-subtracted IR detector signal, in Volts, from the IR5 measurement channel of the GPC instrument, and M_{PE} is the polyethylene-equivalent MW determined from Equation 1. Data calculation were performed using “GPC One software (version 2.013H)” from PolymerChar.

Creep Zero Shear Viscosity Measurement Method

Zero-shear viscosities were obtained via creep tests, which were conducted on an AR-G2 stress controlled rheometer (TA Instruments; New Castle, Del), using “25-mm-diameter” parallel plates, at 190°C. The rheometer oven was set to test temperature for at least 30 minutes, prior to zeroing the fixtures. At the testing temperature, a compression molded sample disk was inserted between the plates, and allowed to come to equilibrium for five minutes. The upper plate was then lowered down to 50 μm (instrument setting) above the desired testing gap (1.5 mm). Any superfluous material was trimmed off, and the upper plate was lowered to the desired gap. Measurements were done under nitrogen purging, at a flow rate of 5 L/min. The default creep time was set for two hours. Each sample was compression-molded into a “2 mm thick x 25 mm diameter” circular plaque, at 177°C, for five minutes, under 10 MPa pressure, in air. The sample

was then taken out of the press and placed on a counter top to cool.

A constant low shear stress of 20 Pa was applied for all of the samples, to ensure that the steady state shear rate was low enough to be in the Newtonian region. The resulting steady state shear rates were in the range from 10^{-3} to 10^{-4} s^{-1} for the samples in this study. Steady state was 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) was creep compliance and t was creep time. If the slope of the linear regression was greater than 0.97, steady state was considered to be reached, then the creep test was stopped. In all cases in this study, the slope meets the criterion within one hour. The steady state shear rate was 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 was strain. The zero-shear viscosity was determined from the ratio of the applied stress to the steady state shear rate.

In order to determine if the sample was degraded during the creep test, a small amplitude oscillatory shear test was 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 were compared. If the difference of the viscosity values, at 0.1 rad/s, was greater than 5%, the sample was considered to have degraded during the creep test, and the result was 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 a linear polyethylene material (see ANTEC proceeding below) at the equivalent weight average molecular weight ($M_w(\text{conv gpc})$), according to the following Equation 5:

$$ZSVR = \frac{\eta_{0B}}{\eta_{0L}} = \frac{\eta_{0B}}{2.29^{-15} M_{w(\text{conv gpc})}^{3.65}} \quad (\text{Eqn. 5}).$$

The ZSV value was obtained from creep test, at 190°C, via the method described above. The $M_w(\text{conv gpc})$ value was determined by the conventional GPC method (Equation 3), as discussed above. The correlation between ZSV of linear polyethylene and its $M_w(\text{conv gpc})$ was established based on a series of linear polyethylene reference materials. A description for the ZSV- M_w relationship can be found in the ANTEC proceeding: Karjala et al., *Detection of Low Levels of Long-chain Branching in Polyolefins*, Annual Technical Conference - Society of Plastics Engineers (2008), 66th 887-891.

¹H NMR Method

A stock solution (3.26 g) was added to “0.133 g of the polymer sample” in 10 mm NMR tube. The stock solution was a mixture of tetrachloroethane-d₂ (TCE) and perchloroethylene (50:50, w:w) with 0.001M Cr³⁺. The solution in the tube was purged with N₂, for 5 minutes, to reduce the amount of oxygen. The capped sample tube was left at room temperature, overnight, to swell the polymer sample. The sample was dissolved at 110°C with periodic vortex mixing. The samples were free of the additives that may contribute to unsaturation, for example, slip agents such as erucamide. Each ¹H NMR analysis was run with a 10 mm cryoprobe, at 120°C, on Bruker AVANCE 400 MHz spectrometer.

Two experiments were run to get the unsaturation: the control and the double presaturation experiments. For the control experiment, the data was processed with an exponential window function with LB=1 Hz, and the baseline was corrected from 7 to -2 ppm. The signal from residual ¹H of TCE was set to 100, and the integral I_{total} from -0.5 to 3 ppm was used as the signal from whole polymer in the control experiment. The “number of CH₂ group, NCH₂,” in the polymer was calculated as follows in Equation 1A:

$$NCH_2 = I_{total}/2 \text{ (Eqn. 1A).}$$

For the double presaturation experiment, the data was processed with an exponential window function with LB=1 Hz, and the baseline was corrected from about 6.6 to 4.5 ppm. The signal from residual ¹H of TCE was set to 100, and the corresponding integrals for unsaturations (I_{vinylene}, I_{trisubstituted}, I_{vinyl} and I_{vinylidene}) were integrated. It is well known to use NMR spectroscopic methods for determining polyethylene unsaturation, for example, see Busico, V., et al., *Macromolecules*, 2005, 38, 6988. The number of unsaturation unit for vinylene, trisubstituted, vinyl and vinylidene were calculated as follows:

$$N_{vinylene} = I_{vinylene}/2 \text{ (Eqn. 2A),}$$

$$N_{trisubstituted} = I_{trisubstituted} \text{ (Eqn. 3A),}$$

$$N_{vinyl} = I_{vinyl}/2 \text{ (Eqn. 4A),}$$

$$N_{vinylidene} = I_{vinylidene}/2 \text{ (Eqn. 5A).}$$

The unsaturation units per 1,000 carbons, all polymer carbons including backbone carbons and branch carbons, were calculated as follows:

$$N_{\text{vinylene}}/1,000C = (N_{\text{vinylene}}/NCH_2) * 1,000 \quad (\text{Eqn. 6A}),$$

$$N_{\text{trisubstituted}}/1,000C = (N_{\text{trisubstituted}}/NCH_2) * 1,000 \quad (\text{Eqn. 7A}),$$

$$N_{\text{vinyl}}/1,000C = (N_{\text{vinyl}}/NCH_2) * 1,000 \quad (\text{Eqn. 8A}),$$

$$N_{\text{vinylidene}}/1,000C = (N_{\text{vinylidene}}/NCH_2) * 1,000 \quad (\text{Eqn. 9A}),$$

5 The chemical shift reference was set at 6.0 ppm for the ^1H signal from residual proton from TCE-d₂. The control was run with ZG pulse, NS=4, DS=12, SWH=10,000 Hz, AQ=1.64s, D1=14s. The double presaturation experiment was run with a modified pulse sequence, with O1P = 1.354 ppm, O2P = 0.960 ppm, PL9 = 57db, PL21 = 70 db, NS = 100, DS = 4, SWH = 10,000 Hz, AQ = 1.64s, D1 = 1 s (where D1 is the presaturation time), D13 = 13s. Only the vinyl levels were reported
10 in Table 2 below.

^{13}C NMR Method

15 Samples are prepared by adding approximately 3g of a 50/50 mixture of tetra-chloroethane-d₂/orthodichlorobenzene, containing 0.025 M Cr(AcAc)₃, to a "0.25 g polymer sample" in a 10 mm NMR tube. Oxygen is removed from the sample by purging the tube headspace with nitrogen. The samples are then dissolved, and homogenized, by heating the tube and its contents to 150°C, using a heating block and heat gun. Each dissolved sample is visually inspected to ensure homogeneity.

20 All data are collected using a Bruker 400 MHz spectrometer. The data is acquired using a 6 second pulse repetition delay, 90-degree flip angles, and inverse gated decoupling with a sample temperature of 120°C. All measurements are made on non-spinning samples in locked mode. Samples are allowed to thermally equilibrate for 7 minutes prior to data acquisition. The ^{13}C NMR chemical shifts were internally referenced to the EEE triad at 30.0 ppm.

25 C13 NMR Comonomer Content: It is well known to use NMR spectroscopic methods for determining polymer composition. ASTM D 5017-96; J. C. Randall et al., in "NMR and Macromolecules" ACS Symposium series 247; J. C. Randall, Ed., Am. Chem. Soc., Washington, D.C., 1984, Ch. 9; and J. C. Randall in "Polymer Sequence Determination", Academic Press, New York (1977) provide general methods of polymer analysis by NMR spectroscopy.

Molecular Weighted Comonomer Distribution Index (MWCDI)

30 A GPC-IR, high temperature chromatographic system from PolymerChar (Valencia, Spain) was equipped with a Precision Detectors' (Amherst, MA) 2-angle laser light scattering detector Model 2040, and an IR5 infra-red detector (GPC-IR) and a 4-capillary viscometer, both from

PolymerChar. The “15-degree angle” of the light scattering detector was used for calculation purposes. Data collection was performed using PolymerChar Instrument Control software and data collection interface. The system was equipped with an on-line, solvent degas device and pumping system from Agilent Technologies (Santa Clara, CA).

5 Injection temperature was controlled at 150 degrees Celsius. The columns used, were four, 20-micron “Mixed-A” light scattering columns from Polymer Laboratories (Shropshire, UK). The solvent was 1,2,4-trichlorobenzene. The samples were prepared at a concentration of “0.1 grams of polymer in 50 milliliters of solvent.” The chromatographic solvent and the sample preparation solvent each contained “200 ppm of butylated hydroxytoluene (BHT).” Both solvent sources were
10 nitrogen sparged. Ethylene-based polymer samples were stirred gently, at 160 degrees Celsius, for three hours. The injection volume was “200 microliters,” and the flow rate was “1 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 g/mole.
15 These standards were arranged in six “cocktail” mixtures, with at least a decade of separation between individual molecular weights. The standards were purchased from Polymer Laboratories (Shropshire UK). 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 g/mole, and at “0.050 grams in 50 milliliters of solvent” for molecular weights less than 1,000,000 g/mole. The polystyrene
20 standards were dissolved at 80 degrees Celsius, with gentle agitation, for 30 minutes. The narrow standards mixtures were run first, and in order of decreasing “highest molecular weight component,” to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1B (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

25
$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (\text{Eqn. 1B}),$$

where M is the molecular weight, A has a value of approximately 0.40 and B is equal to 1.0. The A value was adjusted between 0.385 and 0.425 (depending upon specific column-set efficiency), such that NBS 1475A (NIST) linear polyethylene weight-average molecular weight corresponded to 52,000 g/mole, as calculated by Equation 3B, below:

$$\text{Mn(LALS gpc)} = \frac{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (IR_{\text{measurement channel}_i})}{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} \left(IR_{\text{measurement channel}_i} / M_{PE_i} \right)} \quad (\text{Eqn. 2B})$$

$$\text{Mw(LALS gpc)} = \frac{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (M_{PE_i} IR_{\text{measurement channel}_i})}{\sum_{i=RV_{\text{integration start}}}^{i=RV_{\text{integration end}}} (IR_{\text{measurement channel}_i})} \quad (\text{Eqn. 3B})$$

In Equations 2B and 3B, RV is column retention volume (linearly-spaced), collected at “1 point per second.” The IR is the baseline-subtracted IR detector signal, in Volts, from the measurement channel of the GPC instrument, and the M_{PE} is the polyethylene-equivalent MW determined from Equation 1B. Data calculation were performed using “GPC One software (version 2.013H)” from PolymerChar.

A calibration for the IR5 detector ratios was performed using at least ten ethylene-based polymer standards (polyethylene homopolymer and ethylene/octene copolymers; narrow molecular weight distribution and homogeneous comonomer distribution) of known short chain branching (SCB) frequency (measured by the ^{13}C NMR Method, as discussed above), ranging from homopolymer (0 SCB/1000 total C) to approximately 50 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole, as determined by the GPC-LALS processing method described above. Each standard had a molecular weight distribution (Mw/Mn) from 2.0 to 2.5, as determined by the GPC-LALS processing method described above. Polymer properties for the SCB standards are shown in Table A.

Table A: “SCB” Standards

Wt % Comonomer	IR5 Area ratio	SCB / 1000 Total C	Mw	Mw/Mn
23.1	0.2411	28.9	37,300	2.22
14.0	0.2152	17.5	36,000	2.19
0.0	0.1809	0.0	38,400	2.20
35.9	0.2708	44.9	42,200	2.18
5.4	0.1959	6.8	37,400	2.16
8.6	0.2043	10.8	36,800	2.20
39.2	0.2770	49.0	125,600	2.22
1.1	0.1810	1.4	107,000	2.09
14.3	0.2161	17.9	103,600	2.20
9.4	0.2031	11.8	103,200	2.26

The “IR5 Area Ratio (or “IR5 Methyl Channel Area / IR5 Measurement Channel Area”))” of “the baseline-subtracted area response of the IR5 methyl channel sensor” to “the baseline-subtracted area

response of IR5 measurement channel sensor” (standard filters and filter wheel as supplied by PolymerChar: Part Number IR5_FWM01 included as part of the GPC-IR instrument) was calculated for each of the “SCB” standards. A linear fit of the SCB frequency versus the “IR5 Area Ratio” was constructed in the form of the following Equation 4B:

5
$$\text{SCB/1000 total C} = A_0 + [A_1 \times (\text{IR5 Methyl Channel Area} / \text{IR5 Measurement Channel Area})]$$
 (Eqn. 4B), where A_0 is the “SCB/1000 total C” intercept at an “IR5 Area Ratio” of zero, and A_1 is the slope of the “SCB/1000 total C” versus “IR5 Area Ratio” and represents the increase in the “SCB/1000 total C” as a function of “IR5 Area Ratio.”

10 A series of “linear baseline-subtracted chromatographic heights” for the chromatogram generated by the “IR5 methyl channel sensor” was established as a function of column elution volume, to generate a baseline-corrected chromatogram (methyl channel). A series of “linear baseline-subtracted chromatographic heights” for the chromatogram generated by the “IR5 measurement channel” was established as a function of column elution volume, to generate a baseline-corrected chromatogram (measurement channel).

15 The “IR5 Height Ratio” of “the baseline-corrected chromatogram (methyl channel)” to “the baseline-corrected chromatogram (measurement channel)” was calculated at each column elution volume index (each equally-spaced index, representing 1 data point per second at 1 ml/min elution) across the sample integration bounds. The “IR5 Height Ratio” was multiplied by the coefficient A_1 , and the coefficient A_0 was added to this result, to produce the predicted SCB frequency of the sample. The result was converted into mole percent comonomer, as follows in Equation 5B:

20
$$\text{Mole Percent Comonomer} = \{ \text{SCB}_f / [\text{SCB}_f + ((1000 - \text{SCB}_f * \text{Length of comonomer}) / 2)] \} * 100$$
 (Eqn. 5B),

where “ SCB_f ” is the “SCB per 1000 total C” and the “Length of comonomer” = 8 for octene, 6 for hexene, and so forth.

25 Each elution volume index was converted to a molecular weight value (Mw_i) using the method of Williams and Ward (described above; Eqn. 1B). The “Mole Percent Comonomer (y axis)” was plotted as a function of $\text{Log}(\text{Mw}_i)$, and the slope was calculated between Mw_i of 15,000 and Mw_i of 150,000 g/mole (end group corrections on chain ends were omitted for this calculation). An EXCEL linear regression was used to calculate the slope between, and including, Mw_i from

30 15,000 to 150,000 g/mole. This slope is defined as the molecular weighted comonomer distribution index ($\text{MWCDI} = \text{Molecular Weighted Comonomer Distribution Index}$).

Representative Determination of MWCDI (Inventive First Composition 2)

A plot of the measured “SCB per 1000 total C (= SCB_f)” versus the observed “IR5 Area Ratio” of the SCB standards was generated (see Figure 1), and the intercept (A_0) and slope (A_1) were determined. Here, $A_0 = -90.246$ SCB/1000 total C; and $A_1 = 499.32$ SCB/1000 total C.

5 The “IR5 Height Ratio” was determined for Inventive Example 2 (see integration shown in Figure 2). This height ratio (IR5 Height Ratio of Inventive Example 2) was multiplied by the coefficient A_1 , and the coefficient A_0 was added to this result, to produce the predicted SCB frequency of this example, at each elution volume index, as described above ($A_0 = -90.246$ SCB/1000 total C; and $A_1 = 499.32$ SCB/1000 total C). The SCB_f was plotted as a function of
10 polyethylene-equivalent molecular weight, as determined using Equation 1B, as discussed above. See Figure 3 (Log Mwi used as the x-axis).

The SCB_f was converted into “Mole Percent Comonomer” via Equation 5B. The “Mole Percent Comonomer” was plotted as a function of polyethylene-equivalent molecular weight, as determined using Equation 1B, as discussed above. See Figure 4 (Log Mwi used as the x-axis). A
15 linear fit was from Mwi of 15,000 g/mole to Mwi of 150,000 g/mole, yielding a slope of “2.27 mole percent comonomer x mole/g.” Thus, the MWCDI = 2.27. An EXCEL linear regression was used to calculate the slope between, and including, Mwi from 15,000 to 150,000 g/mole.

Film Testing Conditions

The following physical properties were measured on the films produced (see experimental
20 section).

- **45° Gloss:** ASTM D-2457.
- **Clarity:** ASTM: D-1746.

ASTM D1003 Total Haze

Samples measured for internal haze and overall (total) haze were sampled and prepared
25 according to ASTM D1003. Internal haze was obtained via refractive index matching using mineral oil on both sides of the films. A Hazeguard Plus (BYK-Gardner USA; Columbia, MD) was used for testing. Surface haze was determined as the difference between total haze and internal haze. The total haze was reported as the average of five measurements.

ASTM D1922 MD (Machine Direction) and CD (Cross Direction) Elmendorf Tear Type B

The Elmendorf Tear test determines the average force to propagate tearing through a specified length of plastic film or non rigid sheeting, after the tear has been started, using an Elmendorf-type tearing tester.

- 5 After film production from the sample to be tested, the film was conditioned for at least 40 hours at 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards. Standard testing conditions were 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards.

10 The force, in grams, required to propagate tearing across a film or sheeting specimen was measured using a precisely calibrated pendulum device. In the test, acting by gravity, the pendulum swung through an arc, tearing the specimen from a precut slit. The specimen was held on one side by the pendulum and on the other side by a stationary member. The loss in energy by the pendulum was indicated by a pointer or by an electronic scale. The scale indication was a function of the force required to tear the specimen.

15 The sample specimen geometry used in the Elmendorf tear test was the 'constant radius geometry' as specified in ASTM D1922. Testing is typically carried out on specimens that have been cut from both the film MD and CD directions. Prior to testing, the film specimen thickness was measured at the sample center. A total of 15 specimens per film direction were tested, and the average tear strength and average thickness reported. The average tear strength was normalized to the average thickness.

20 **ASTM D882 MD and CD, 1% and 2% Secant Modulus, Tensile Strength, and Break Strain**

25 The film MD (Machine Direction) and CD (Cross Direction) secant modulus and tensile break strength (or tensile strength) were measured with an Instron universal tester according to ASTM D882-10. The reported secant modulus value was the average of five measurements. The tensile break strength was determined using five film samples in each direction, with each sample being "1 inch x 6 inches" in size. The break strength is the tensile load or force required to rupture or break a given material. It is measured as pounds of force for each square inch (psi). The break strain is the strain at which the material breaks and is measured as length at break divided by original length multiplied by 100 (%).

Puncture Strength

30 The Puncture test determines the resistance of a film to the penetration of a probe at a standard low rate, a single test velocity. The puncture test method is based on ASTM D5748. After

film production, the film was conditioned for at least 40 hours at 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards. Standard testing conditions were 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards. Puncture was measured on a tensile testing machine. Square specimens were cut from a sheet to a size of “6 inches by 6 inches.” The specimen was clamped in a “4 inch
5 diameter” circular specimen holder, and a puncture probe was pushed into the centre of the clamped film at a cross head speed of 10 inches/minute. The internal test method follows ASTM D5748, with one modification. It deviated from the ASTM D5748 method, in that the probe used was a “0.5 inch diameter” polished steel ball on a “0.25 inch” support rod (rather than the 0.75 inch diameter, pear shaped probe specified in D5748).

10 There was a “7.7 inch” maximum travel length to prevent damage to the test fixture. There was no gauge length; prior to testing, the probe is as close as possible to, but not touching the specimen.

A single thickness measurement was made in the centre of the specimen. For each specimen, the maximum force, the force at break, the penetration distance, and the energy to break were
15 determined. A total of five specimens were tested to determine an average puncture value. The puncture probe was cleaned using a "Kim-wipe" after each specimen.

ASTM D1709 Dart Drop

The film Dart Drop test determines the energy that causes a plastic film to fail, under specified conditions of impact by a free falling dart. The test result is the energy, expressed in terms
20 of the weight of the missile falling from a specified height, which would result in the failure of 50% of the specimens tested.

After the film was produced, it was conditioned for at least 40 hours at 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards. Standard testing conditions are 23°C (+/- 2°C) and 50% R.H (+/- 5), as per ASTM standards.

25 The test result was reported as either by Method A, which uses a 1.5” diameter dart head and 26” drop height, or by Method B, which uses a 2” diameter dart head and 60” drop height. The sample thickness was measured at the sample center, and the sample then clamped by an annular specimen holder with an inside diameter of 5 inches. The dart was loaded above the center of the sample, and released by either a pneumatic or electromagnetic mechanism.

30 Testing was carried out according to the ‘staircase’ method. If the sample failed, a new sample was tested with the weight of the dart reduced by a known and fixed amount. If the sample

did not fail, a new sample was tested with the weight of the dart increased by a known amount. After 20 specimens had been tested, the number of failures was determined. If this number was 10, then the test is complete. If the number was less than 10, then the testing continued, until 10 failures had been recorded. If the number was greater than 10, testing continued, until the total of non-

5 failures was 10. The Dart Drop strength was determined from these data, as per ASTM D1709, and expressed in grams, as either the Dart Drop Impact of Type A or Type B. In some cases, the sample Dart Drop Impact strength may lie between A and B. In these cases, it was not possible to obtain a quantitative dart value.

Water Vapor Transmission Rate (WVTR)

10 Water Vapor Transmission Rate (or WVTR) is the absolute transmission rate. WVTR was determined according to ASTM D-6701 and is reported in units of $\text{g/m}^2/\text{day}$.

EXAMPLES

The following examples illustrate the present invention, but are not intended to limit the scope of the invention.

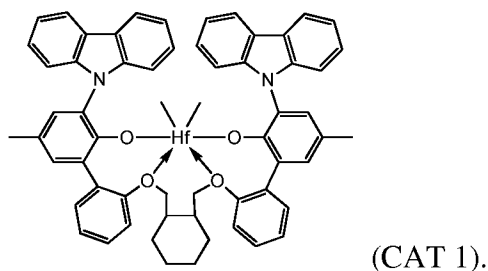
15 EXAMPLE 1:

Inventive First Compositions 1, 2 and 3

Inventive first compositions 1, 2 and 3, each contain two ethylene-octene copolymers. Each composition was prepared, via solution polymerization, in a dual series loop reactor system according to U.S. Pat. No. 5,977,251 (see Figure 2 of this patent), in the presence of a first catalyst system, as described below, in the first reactor, and a second catalyst system, as described below, in

20 the second reactor.

The first catalyst system comprised a bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxyethyl)-methylene-1,2-cyclohexanediylhafnium (IV) dimethyl, represented by the following formula (CAT 1):



25 The molar ratios of the metal of CAT 1, added to the polymerization reactor, in-situ, to that of Cocat1 (modified methyl aluminoxane), or Cocat2 (bis(hydrogenated tallow alkyl)methyl,

tetrakis(pentafluorophenyl)borate(1-) amine), are shown in Table 1.

The second catalyst system comprised a Ziegler-Natta type catalyst (CAT 2). 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 EtAlCl₂ in heptane, and a solution of Ti(O-*i*Pr)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. An aliquot of this composition was further diluted with ISOPAR-E to yield a final concentration of 500 ppm Ti in the slurry. While being fed to, and prior to entry into, the polymerization reactor, the catalyst premix was contacted with a dilute solution of Et₃Al, in the molar Al to Ti ratio specified in Table 1, to give the active catalyst.

The polymerization conditions for the inventive first compositions 1, 2 and 3 are reported in Table 1. As seen in Table 1, Cocat. 1 (modified methyl aluminoxane (MMAO)); and Cocat. 2 (bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) amine) were each used as a cocatalyst for CAT 1. Additional properties of the inventive compositions 1, 2 and 3 were measured, and are reported in Table 2. The GPC MWD profiles, and corresponding comonomer distribution overlays, are shown in Figures 8-10. Each polymer composition was stabilized with minor (ppm) amounts of stabilizers.

Comparative First Compositions A and B

Comparative compositions A and B, each contain two ethylene-octene copolymers, and each was prepared, via solution polymerization, in a dual loop reactor system, in the presence of a first catalyst system, as described below, in the first reactor, and a second catalyst system, as described below, in the second reactor. The first catalyst system comprised titanium, [*N*-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,3a,8a- η)-1,5,6,7-tetrahydro-2-methyl-*s*-indacen-1-yl]silanaminato(2-)- κ N][(1,2,3,4- η)-1,3-pentadiene]- (CAT 3, a constrained geometry catalyst). The second catalyst system comprised the Ziegler-Natta premix (CAT 2), as discussed above.

The polymerization conditions for comparative compositions A and B are reported in Table 1. As seen in Table 1, Cocat. 1 (modified methyl aluminoxane (MMAO)) and Cocat. 2 (bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) amine) were each used as cocatalyst for CAT 3. Additional properties of the comparative compositions A and B were measured, and are reported in Table 2. The GPC MWD profiles, and corresponding comonomer

distribution overlays, are shown in Figures 8 and 9. Each polymer composition was stabilized with minor (ppm) amounts of stabilizers.

Comparative C (First Composition)

Comparative C is an ethylene-hexene copolymer composition, commercially available under the commercial designation EXCEED 1018CA from EXXONMOBIL Chemical Company, and having a density of approximately 0.918 g/cm³, a melt index (I₂ or I₂), measured at 190°C and 2.16 kg, of approximately 1.0 g/10 minutes. Additional properties of the comparative example C were measured, and are reported in Table 2. The GPC MWD profile, and corresponding comonomer distribution overlay, is shown in Figure 8.

Comparative D (First Composition)

Comparative D is an ethylene-octene copolymer composition, provided by The Dow Chemical Company, under the commercial designation ELITE 5230G, and having a density of approximately 0.916 g/cm³, a melt index (I₂ or I₂), measured at 190°C and 2.16 kg, of approximately 4.0 g/10 minutes. Additional properties of the comparative example D were measured, and are reported in Table 2. The GPC MWD profile, and corresponding comonomer distribution overlay, is shown in Figure 10.

Table 1: Polymerization Conditions (Rx1 = reactor 1; Rx2 = reactor 2)

Sample #	Units	Inv. First 1	Inv. First 2	Inv. First 3	Comp. First A	Comp. First B
Reactor Configuration		Dual Series	Dual Series	Dual Series	Dual Series	Dual Series
Comonomer		1-octene	1-octene	1-octene	1-octene	1-octene
<i>REACTOR FEEDS</i>						
First Reactor Total Solvent Flow	lb/hr	1122	1057	1177	958	1061
First Reactor Total Ethylene Flow	lb/hr	190	175	269	184	187
First Reactor Total Comonomer Flow	lb/hr	74	48	118	97	58
First Reactor Hydrogen Feed Flow	SCCM	6827	5017	22848	525	857
Second Reactor Total Solvent Flow	lb/hr	384	451	421	494	561
Second Reactor Total Ethylene Flow	lb/hr	173	204	155	182	216
Second Reactor Total Comonomer Flow	lb/hr	12	8	22	50	17
Second Reactor Hydrogen Feed Flow	SCCM	298	99	100	2446	3829
<i>REACTION</i>						

First Reactor Control Temperature	°C	140	150	143	145	135
First Reactor Ethylene Conversion	%	86.7	90.5	72.7	69.4	77.7
First Reactor Viscosity	cP	2400	2315	824	891	1318
Second Reactor Control Temperature	°C	195	195	190	190	195
Second Reactor Ethylene Conversion	%	87.1	86	87.8	89.2	88.8
Second Reactor Viscosity	cP	869	876	264	892	848
<i>CATALYST</i>						
First Reactor Catalyst	type	CAT 1	CAT 1	CAT 1	CAT 3	CAT 3
First Reactor Catalyst Efficiency	g polymer per g catalyst metal	3,681,068	2,333,579	481,051	2,984,071	2,653,724
First Reactor Cocatalyst (Cocat. 2) to Catalyst Metal Molar Ratio	Ratio	1.3	1.8	1.2	1.2	1.5
First Reactor Cocatalyst (Cocat. 1) to Catalyst Metal Molar Ratio	Ratio	20	100	5	15	25
Second Reactor Catalyst Efficiency	g polymer per g catalyst metal	404,385	469,511	176,500	561,063	390,994
Second Reactor Al to Ti Molar Ratio	Ratio	4.0	4.0	1.2	4.0	4.0

* solvent = ISOPAR E

Table 2: Properties of Inventive and Comparative Compositions

	Unit	Inv. First 1	Inv. First 2	Inv. First 3	Comp. First A	Comp. First B	Comp. First C	Comp. First D
Density	g/cc	0.9174	0.9245	0.9148	0.9162	0.9253	0.9191	0.9158
I ₂	g/10 min	0.83	0.87	3.91	0.93	0.80	0.95	4.05
I ₁₀ /I ₂		7.7	8.0	7.3	8.2	8.4	6.0	7.0
7.0 – 1.2xlog(I ₂)		7.1	7.1	6.3	7.0	7.1	7.0	6.3
Mn (conv.gpc)	g/mol	32,973	33,580	20,244	33,950	34,626	45,645	26,355
Mw (conv.gpc)		117,553	117,172	78,820	111,621	112,688	109,931	76,118
Mz (conv.gpc)		270,191	277,755	186,520	258,547	254,301	197,425	155,254
Mw/Mn (conv.gpc)		3.57	3.49	3.89	3.29	3.25	2.41	2.89
Mz/Mw (conv.gpc)		2.30	2.37	2.37	2.32	2.26	1.80	2.04
Eta* (0.1 rad/s)	Pa·s	9,496	11,231	1,997	10,342	11,929	6,975	2,057
Eta* (1.0 rad/s)	Pa·s	7,693	8,455	1,920	7,313	7,942	6,472	1,908
Eta* (10 rad/s)	Pa·s	4,706	4,977	1,527	4,337	4,586	5,071	1,473

Eta* (100 rad/s)	Pa•s	1,778	1,893	792	1,769	1,873	2,415	834
Eta*0.1/ Eta*100		5.34	5.93	2.52	5.85	6.37	2.89	2.47
Eta zero	Pa•s	11,210	13,947	2,142	12,994	15,661	7,748	2,176
MWCDI		2.64	2.27	1.56	0.65	0.79	-0.06	-0.54
Vinyls	Per 1000 total Carbons	134	179	115	157	148	69	56
ZSVR		1.53	1.92	1.25	2.13	2.49	1.35	1.45

EXAMPLE 2:**Inventive Compositions 4 and 5**

5 Inventive compositions 4 and 5 each contain an ethylene-octene copolymer. Inventive compositions 4 and 5 were prepared in the same manner and using the same catalyst system as inventive compositions 1-3, with the exception of the polymerization conditions which are reported in Table 3.

Table 3: Polymerization Conditions (Rx1 = reactor 1; Rx2 = reactor 2)

Sample #	Units	Inv. Comp. 4	Inv. Comp. 5
Reactor Configuration		Dual Series	Dual Series
Comonomer		1-octene	1-octene
<i>REACTOR FEEDS</i>			
First Reactor Total Solvent Flow	lb/hr	1323	957
First Reactor Total Ethylene Flow	lb/hr	228	200
First Reactor Total Comonomer Flow	lb/hr	86	71
First Reactor Hydrogen Feed Flow	SCCM	6379	4578
Second Reactor Total Solvent Flow	lb/hr	525	464
Second Reactor Total Ethylene Flow	lb/hr	201	211
Second Reactor Total Comonomer Flow	lb/hr	12	13
Second Reactor Hydrogen Feed Flow	SCCM	4392	2233
<i>REACTION</i>			
First Reactor Control Temperature	°C	165	165
First Reactor Ethylene Conversion	%	89.0	92.0
First Reactor Viscosity	cP	402	1121
Second Reactor Control	°C	195	195

Temperature			
Second Reactor Ethylene Conversion	%	86.2	84.7
Second Reactor Viscosity	cP	219	524.7
<i>CATALYST</i>			
First Reactor Catalyst	type	CAT 1	CAT 1
First Reactor Catalyst Efficiency	g polymer per g catalyst metal	617060	1204000
First Reactor Cocatalyst (Cocat. 2) to Catalyst Metal Molar Ratio	Ratio	1.2	1.2
First Reactor Cocatalyst (Cocat. 1) to Catalyst Metal Molar Ratio	Ratio	18.0	50.0
Second Reactor Catalyst Efficiency	g polymer per g catalyst metal	354157	422627
Second Reactor Al to Ti Molar Ratio	Ratio	4.0	4.0

* solvent = ISOPAR E

A breathable film was formed from Inventive Composition 4. Inventive Composition 4 was compounded using a Farrel continuous mixer with underwater pelletization. The amounts of the components that were compounded into pellets are shown in Table 4:

Table 4

Component	Weight Percent
Inventive Composition 4	50%
Calcium Carbonate	45%
LDPE	5%

The Calcium Carbonate was Imerys FilmLink® 500, which is commercially available from Imerys Carbonates. The LDPE was DOW™ LDPE 640I, which is commercially available from The Dow Chemical Company.

Films were fabricated on a 5 layer Egan Davis Standard coextrusion cast film line. The cast line consisted of three 2-1/2" and two 2" 30:1 L/D Egan Davis Standard MAC extruders which are air cooled. All extruders had moderate work DSB (Davis Standard Barrier) type screws. Equipment specifications included a Cloeren 5 layer dual plane feed block and a Cloeren 36" Epich II autogage 5.1 die. The primary chill roll had a matte finish and was 40" outer diameter (O.D.) x 40" long with

a 30-40 RMS surface finish for improved release characteristics. The secondary chill roll was 20" O.D. x 40" long with a 2-4 RMS surface for improved web tracking. Both the primary and secondary chill rolls had chilled water circulating through them to provide quenching. A Scantech X-ray gauge sensor for gauge thickness and automatic gauge control was available if needed. Films were fabricated at following conditions: Melt temperature = 400°F; Temperature profile (B1 300°F, B2 400°F, B3-5 400°F, Screen 400°F, Adaptor 400°F, Die all zones 400°F), Throughput rate = 200-270 lb/hr, Chill roll temperature = 70° F, Cast roll temperature = 70° F, Air knife = 7.4" H₂O, Vacuum box=OFF, Die gap = 20-25 mil, and Air gap = 4".

Each film was oriented using a Machine Direction Orientation (MDO) System, such as those available from Marshall and Williams Plastics and Parkinson Technologies, Inc. The film was oriented in the machine direction using a series of rollers at the same or different speeds to impart orientation. The film roll width on the feed roller was 24 inches with a thickness of 2.0 mil. The rollers were kept at the following temperatures: preheat roller 1 (165° F), preheat roller 2 (165° F), slow draw roller (185° F), fast draw roller (175° F), anneal roller (165° F) and cold roller (140° F). The speed of the slow draw roll was 5.1 feet per minute, and the speed of the fast draw roll was 19.1 feet per minute to provide a draw ratio of 3.75. The exit width of the film roll was 21.6 inches with a thickness of 0.7 – 0.8 mil. The temperature profile used in the MDO System is shown in Table 5:

Table 5

Preheat 1	Preheat 2	Slow Draw	Fast Draw	Anneal	Cool
165° F	165° F	185° F	175° F	165° F	140° F

Various film properties of the oriented film were measured. The number of samples, average values, and standard deviations are shown in Table 6:

Table 6

Property	# of Samples	Average $\pm$ Std. Dev.
Elmendorf Tear, Machine Direction (gram force)	15	3.6 $\pm$ 1.2
Elmendorf Tear, Cross Direction (gram force)	15	525 $\pm$ 81
Break Stress, Machine Direction (psi)	5	4835 $\pm$ 1993
Break Stress, Cross Direction (psi)	5	954 $\pm$ 41
Break Strain, Machine Direction (%)	5	51 $\pm$ 9
Break Strain, Cross Direction (%)	5	493 $\pm$ 25
Puncture Strength (ft*lb/in ³)	5	7.6 $\pm$ 1.9
WVTR (g/m ² /day)	2	2350 $\pm$ 44

EXAMPLE 3:

The stretch windows of Inventive Composition 4 and DOWLEX™ 2047G Polyethylene resin (commercially available from The Dow Chemical Company) were determined using MDO conditions as described above with modification of the roll temperatures as shown in Table 7:

Table 7

Preheat 1	Preheat 2	Slow Draw	Fast Draw	Anneal	Cool
165° F	185° F	205° F	195° F	165° F	140° F

The stretch windows are shown in Table 8:

Table 8

Resin	Minimum Draw Ratio	Maximum Draw Ratio
Inventive Composition 4	3.25	5.75
DOWLEX™ 2047G	3.50	5.25

The minimum draw ratio was the draw ratio where haze variations (tiger striping) were visually absent from the film, and the maximum draw ratio was the draw ratio where pinholes or breaks in the film web were observed.

EXAMPLE 4:**Inventive Compositions 6 and 7**

Inventive compositions 6 and 7 each contain an ethylene-octene copolymer. Inventive compositions 6 and 7 were prepared in the same manner and using the same catalyst system as inventive compositions 1-3, with the exception of the polymerization conditions which are reported in Table 9.

Table 9: Polymerization Conditions (Rx1 = reactor 1; Rx2 = reactor 2)

Sample #	Units	Inv. Comp. 6	Inv. Comp. 7
Reactor Configuration		Dual Series	Dual Series
Comonomer		1-octene	1-octene
<i>REACTOR FEEDS</i>			
First Reactor Total Solvent Flow	lb/hr	965	724
First Reactor Total Ethylene Flow	lb/hr	201	151
First Reactor Total Comonomer Flow	lb/hr	49	23
First Reactor Hydrogen Feed Flow	SCCM	6092	4057
Second Reactor Total Solvent Flow	lb/hr	492	641
Second Reactor Total Ethylene Flow	lb/hr	223	291
Second Reactor Total Comonomer Flow	lb/hr	10	8
Second Reactor Hydrogen Feed Flow	SCCM	1786	4002
<i>REACTION</i>			
First Reactor Control Temperature	°C	160	160
First Reactor Ethylene Conversion	%	91.6	93.0
First Reactor Viscosity	cP	1620	2186
Second Reactor Control Temperature	°C	195	195
Second Reactor Ethylene Conversion	%	85.8	88.3
Second Reactor Viscosity	cP	579.2	775.7
<i>CATALYST</i>			
First Reactor Catalyst	type	CAT 1	CAT 1
First Reactor Catalyst Efficiency	g polymer per g catalyst metal	2610844	2461080
First Reactor Cocatalyst (Cocat. 2) to Catalyst Metal Molar Ratio	Ratio	1.3	1.2
First Reactor Cocatalyst (Cocat. 1) to Catalyst Metal Molar Ratio	Ratio	50.0	50.0
Second Reactor Catalyst Efficiency	g polymer per g catalyst metal	622016	741104

Second Reactor Al to Ti Molar Ratio	Ratio	4.0	4.0
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Properties of the Inventive Compositions were measured, and are reported in Table 10.

Table 10: Properties of Inventive Compositions

	Unit	Inv. Comp. 6	Inv. Comp. 7	
Density	g/cc	0.9244	0.9351	
I ₂	g/10 min	2.31	2.61	
I ₁₀ /I ₂		7.5	7.5	
7.0 – 1.2xlog(I ₂)		6.6	6.5	
Mn (conv.gpc)	g/mol	30,905	29,269	
Mw (conv.gpc)	g/mol	93,984	88,988	
Mz (conv.gpc)	g/mol	223,635	204,901	
Mw/Mn (conv.gpc)		3.04	3.04	
Mz/Mw (conv.gpc)		2.38	2.30	
Eta* (0.1 rad/s)	Pa•s	3,876	3,308	
Eta* (1.0 rad/s)	Pa•s	3,356	2,869	
Eta* (10 rad/s)	Pa•s	2,337	2,028	
Eta* (100 rad/s)	Pa•s	1,107	1,000	
Eta*0.1/ Eta*100		3.50	3.31	
MWCDI		1.80	1.23	

5

Breathable films can be formed from Inventive Compositions 6 and 7.

That which is claimed:

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1. A breathable film comprising a first composition, wherein the first composition comprises at least one ethylene-based polymer and wherein the first composition comprises a MWCDI value greater than 0.9, and a melt index ratio (I10/I2) that meets the following equation: $I10/I2 \geq 7.0 - 1.2 \times \log(I2)$.

5

2. The breathable film of claim 1, wherein the breathable film further comprises 40 to 65 weight percent of a mineral filler.

3. The breathable film of claim 1 or claim 2, wherein the first composition has a MWCDI value less than, or equal to, 10.0.

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4. The breathable film of any of the preceding claims, wherein the first composition has a density of 0.910 to 0.940 g/cm³ and a melt index (I2) of 0.5 to 30 g/10 minutes.

5. The breathable film of any of the preceding claims, wherein the film has a basis weight of 10 to 20 g/m².

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6. The breathable film of any of the preceding claims, further comprising a second polymer, and wherein the second polymer is selected from the following: a LLDPE, a VLDPE, a LDPE, a MDPE, a HDPE, a HMWHDPE, a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate, a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof.

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7. The breathable film of any of the preceding claims, wherein the breathable film comprises a first layer comprising the first composition, and a second layer, wherein the second layer comprises a polymer selected from the following: the first composition, a LLDPE, a VLDPE, a LDPE, a MDPE, a HDPE, a HMWHDPE, a propylene-based polymer, a polyolefin plastomer, a polyolefin elastomer, an olefin block copolymer, an ethylene vinyl acetate, an ethylene acrylic acid, an ethylene methacrylic acid, an ethylene methyl acrylate, an ethylene ethyl acrylate, an ethylene butyl acrylate,

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a polyisobutylene, a maleic anhydride-grafted polyolefin, an ionomer of any of the foregoing, or a combination thereof.

8. The breathable film of any of the preceding claims, wherein the breathable film comprises at
5 least 30 weight percent of the first composition.
9. The breathable film of any of the preceding claims, wherein the breathable film exhibits a water vapor transmission rate of at least 500 g/m²-day-atm and up to 10,000 g/m²-day-atm.
- 10 10. The breathable film of any of the preceding claims, wherein the breathable film is oriented in at least one of the machine direction and the cross direction.
11. The breathable film of any of the preceding claims, wherein the breathable film is oriented in the machine direction and the cross direction.
15
12. A laminate comprising the breathable film of any of the preceding claims.
13. The laminate of claim 12, further comprising a non-woven material.
- 20 14. An article comprising the laminate of claim 12 or claim 13.
15. An article comprising the breathable film of any of claims 1-11.

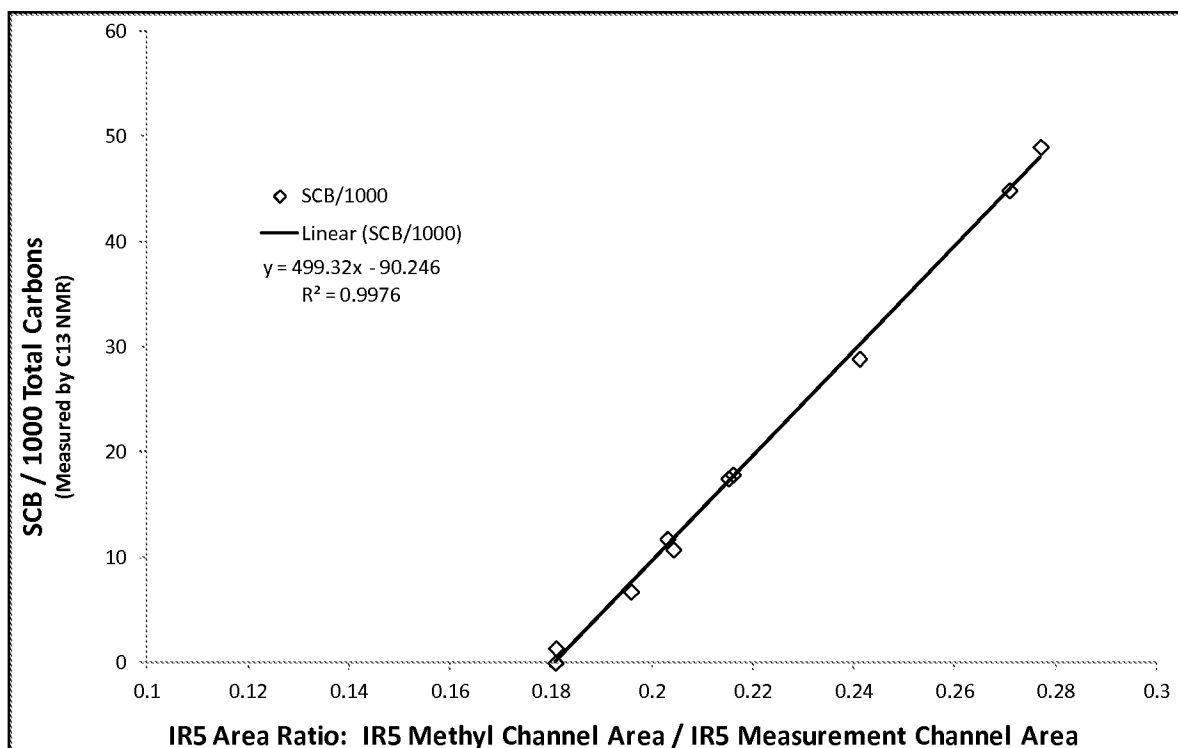


FIGURE 1

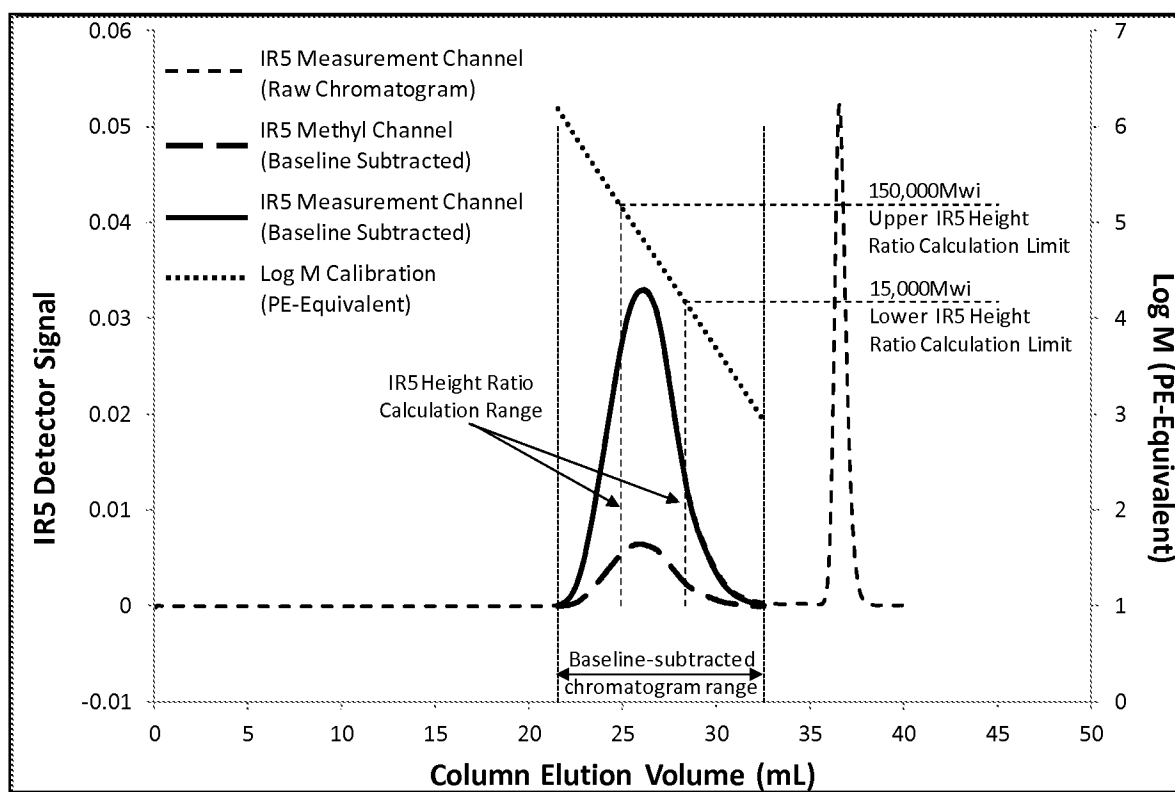


FIGURE 2

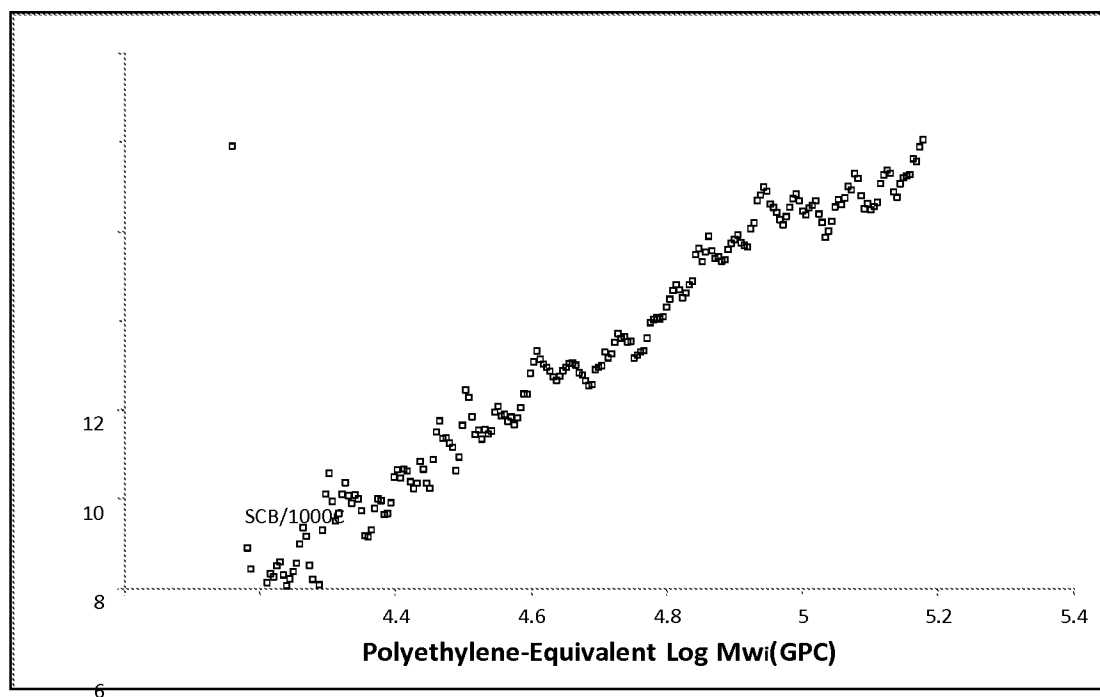


FIGURE 3

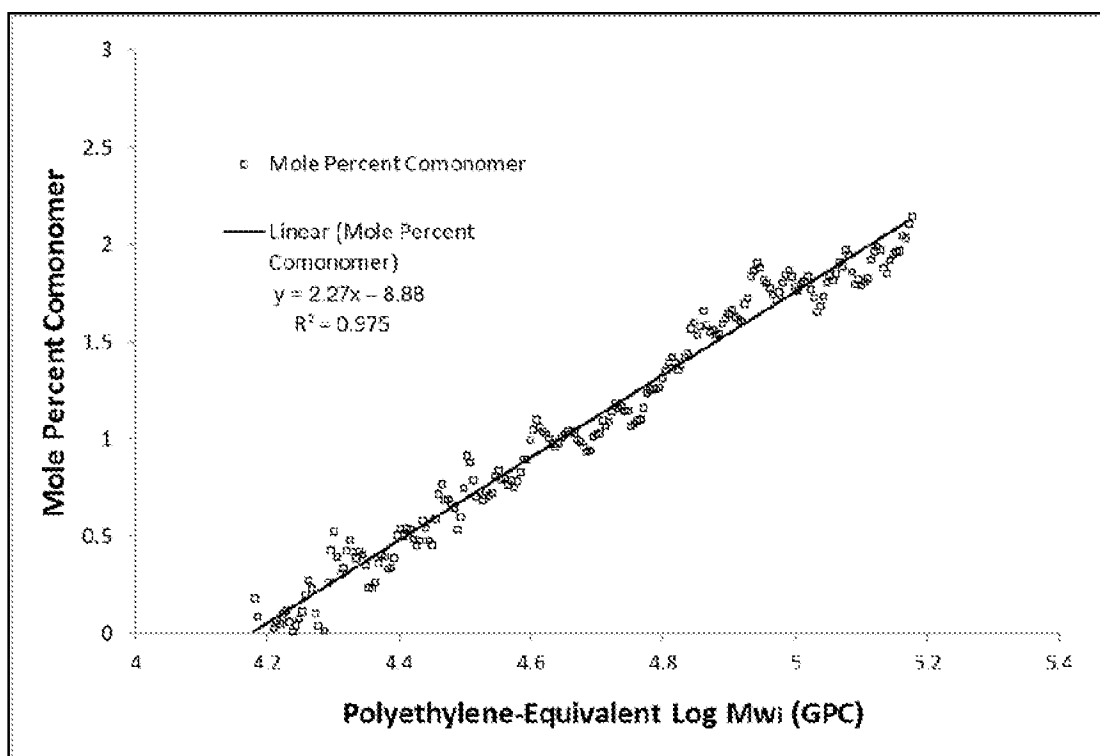


FIGURE 4

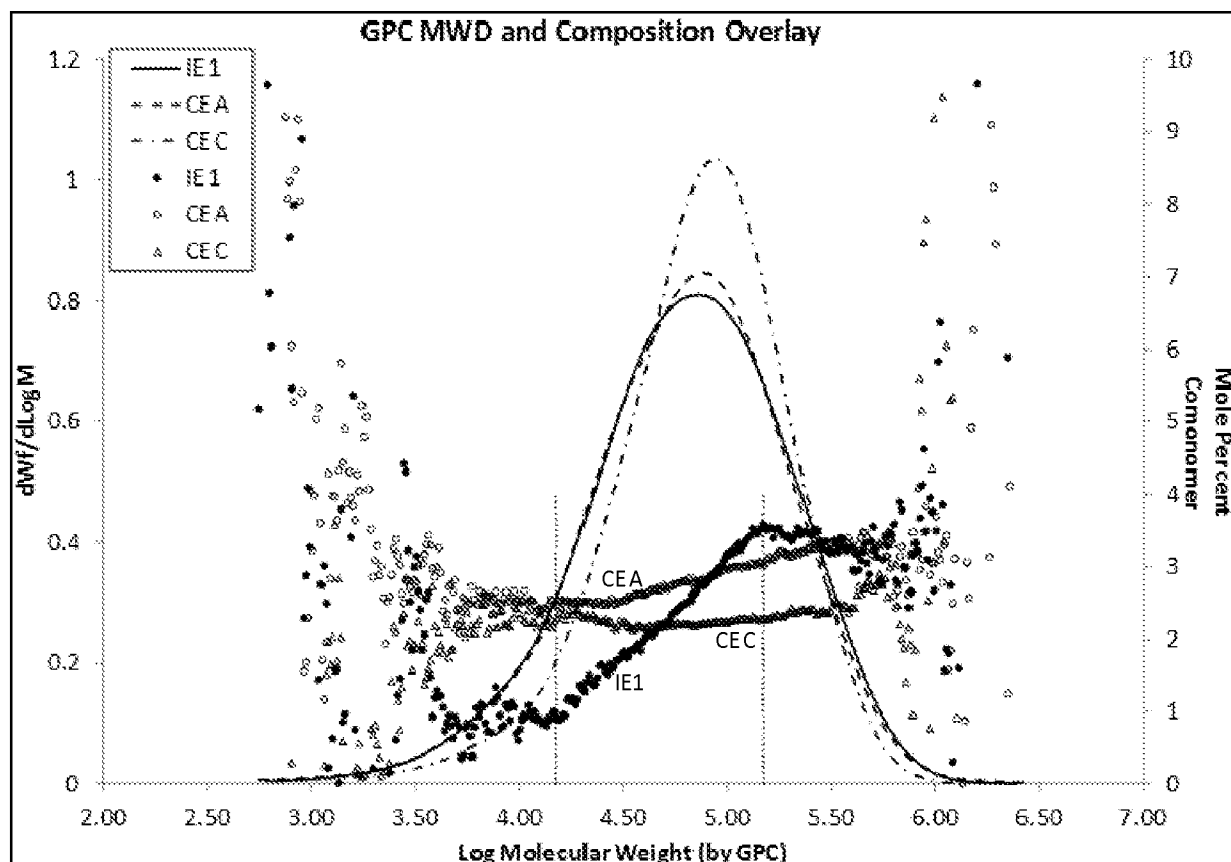


FIGURE 5

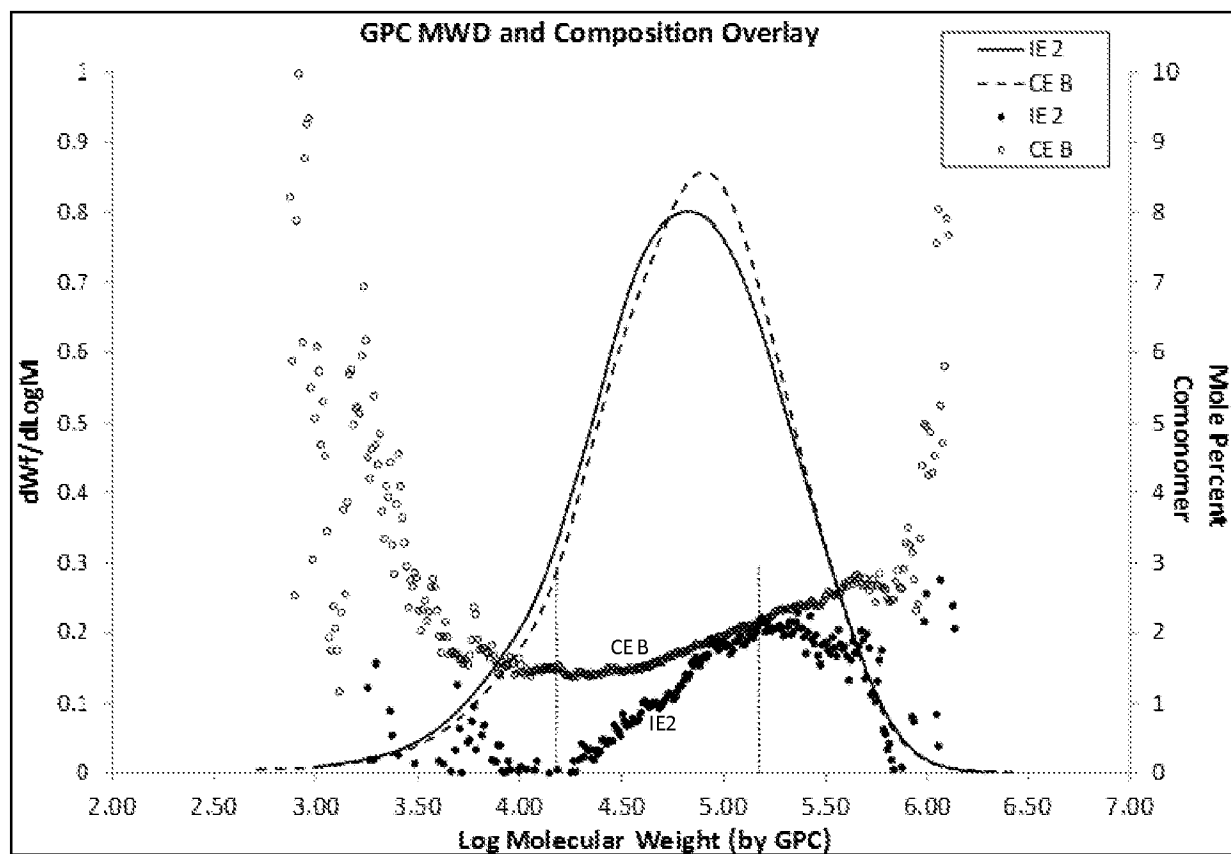
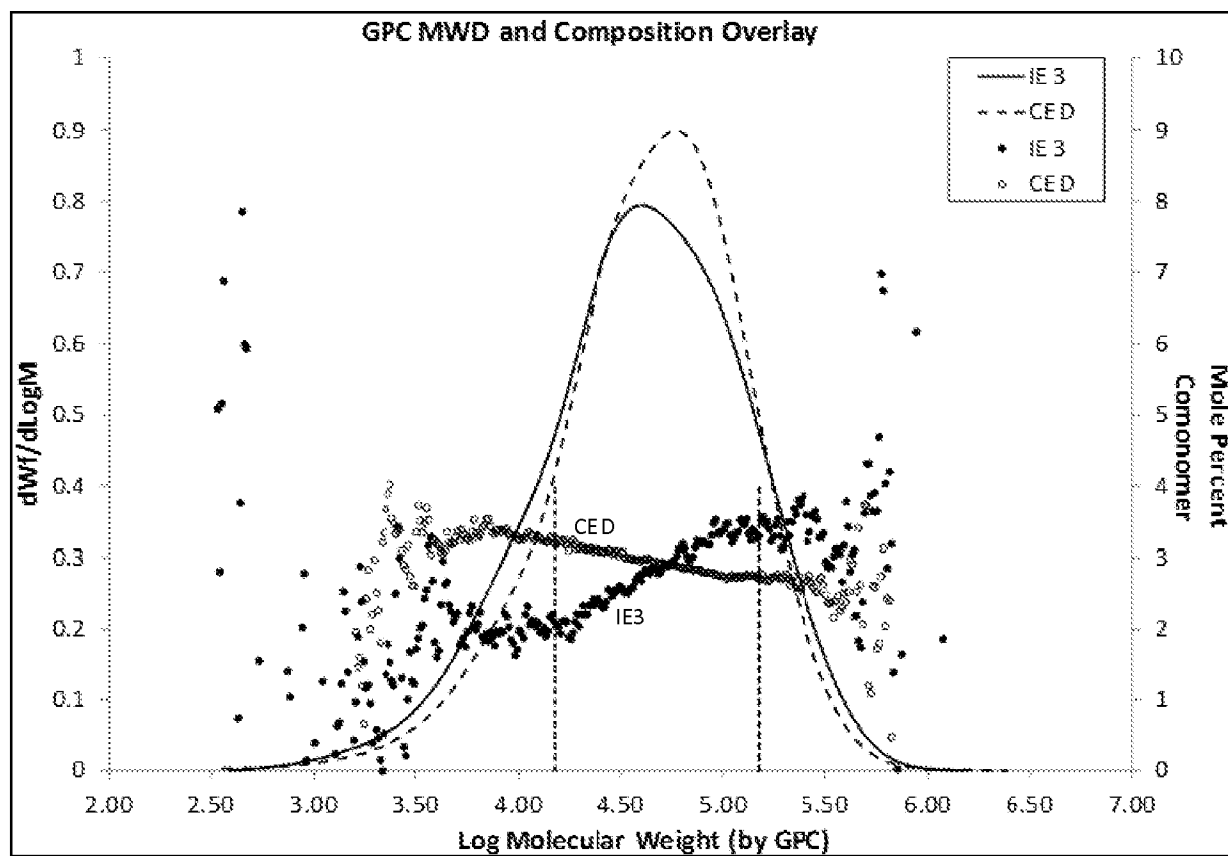


FIGURE 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/037870

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B27/06 B32B27/32 C08F210/16 C08F4/64 C08L23/08
B32B27/20

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/058639 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 17 April 2014 (2014-04-17) cited in the application examples cpc2, ipc5; tables 1a, 1b -----	1-15
Y	WO 2012/061168 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; DEMIRORS MEHMET [US]; CONG RONGJUAN) 10 May 2012 (2012-05-10) examples C, D; table 1 -----	1-15
Y	US 2013/046061 A1 (HERMEL-DAVIDOCK THERESA J [US] ET AL) 21 February 2013 (2013-02-21) example Inv.Ex4; tables 3-5 -----	1-15
Y	WO 2013/052636 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 11 April 2013 (2013-04-11) examples Inv.Ex.2,3,5; table 1 ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

15 September 2015

Date of mailing of the international search report

22/09/2015

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Balmer, J

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/037870

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 375 584 A1 (BOREALIS TECH OY [FI]) 2 January 2004 (2004-01-02) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/037870

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 2014058639	A1	17-04-2014	CN	104837627 A		12-08-2015
			EP	2906423 A1		19-08-2015
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