NARROW MWD, COMPOSITIONALLY OPTIMIZED ETHYLENE INTERPOLYMER COMPOSITION, PROCESS FOR MAKING THE SAME AND ARTICLE MADE THEREFROM

This invention relates to an ethylene interpolymer composition comprised of at least two dominant polymer components, wherein the composition is characterized as having a relatively narrow molecular weight distribution (MWD) and a variably optimized compositional uniformity. The invention also relates to a process for making such a composition and fabricated articles made from the novel composition. The novel composition exhibits improved and balanced toughness properties, good processibility and improved optical properties and is particularly well-suited for use in applications such as trash can liners, lamination films, oriented shrink film and bags, overwrap films, and heavy duty shipping bags, especially as blown films.

In the manufacture of ethylene interpolymers such as ethylene interpolymerized with at least one unsaturated comonomer, a number of polymerization methods and procedures are known. For example, single site and constrained geometry catalyst systems have been disclosed for manufacturing olefin polymers with high compositional uniformity and relatively narrow molecular weight distributions.

Variations in the reactor systems used to manufacture ethylene interpolymers are also known. For example, while single site catalysis systems are disclosed to provide compositionally uniform, narrow MWD products (for example, EXACT plastomers supplied commercially by Exxon Chemical Corporation) when employed in a high pressure polymerization system and conversely products with decreased homogeneity with respect to the short chain branching distribution and a broader molecular weight distribution (for example, EXCEED resins supplied commercially by Exxon Chemical Corporation) when employed in a low pressure gas phase polymerization process.

This Sheet Has Been Replaced

While the art is replete with various products and manufacturing techniques, the known range of manufacturing capabilities still do not permit the manufacturing of ethylene interpolymer compositions characterized as having high, balanced toughness properties, good processability and improved optical properties. That is, known ethylene interpolymer compositions (either as single reactor products, multiple reactor products or polymer blends) do not exhibit the desired balance of good processability (that is, sufficient extrusion processing characteristics to avoid, for example, excessively high extruder amperage during blown film fabrication with sufficient melt strength to permit, for example, good bubble stability to maximize output rates); balanced tear resistance; high and balanced tensile properties; high dart impact resistance; and low film haze.

The traditional polyethylene solution for achieving improved toughness properties involves manufacturing products with narrow molecular weight distributions as broad molecular weight distributions are known to yield reduced toughness properties. Beyond providing a narrow molecular weight distribution, linear polyethylenes are known to provide improved toughness properties relative to highly branched LDPE. Further, beyond merely a narrow molecular weight distribution and a linear polymer backbone, compositional uniformity has been offered for enhanced toughness properties. However, while the combination of a narrow molecular weight distribution, a linear polymer backbone and compositional uniformity may provide enhanced toughness, this combination of polymer properties invariably provides poor processability (for example, excessively high extruder amperage).

In contrast to the combination of a narrow molecular weight distribution, increased compositional uniformity and a linear polymer backbone, to achieve the balance of good processability (that is, resistance to melt fracture and improved melt strength) and toughness properties, Lai et al.

This Sheet Has Been Replaced



disclose in U.S. Patent No. 5,272,236 substantially linear ethylene polymers characterized as having narrow molecular weight distribution, high compositional uniformity and long chain branching.

Other proposed solutions for achieving balanced properties include polymer blends such as those disclosed by Kale et al. in US Patent Number 5,210,142 and Hazlitt et al. in US Patent Number 5,370,940. However, while such polymer blends exhibit good handling properties and processability, known polymer blends inevitably exhibit insufficient compositional uniformity to provide the desired balanced toughness properties.

Fraser et al. in U.S. Patent No. 4,243,619 disclose a process for making film from a narrow molecular weight distribution ethylene/α-olefin copolymer composition prepared by a Ziegler catalyst system which is said to exhibit good optical and mechanical properties.

Research Disclosure No. 310163 (Anonymous) teaches blends comprising a Ziegler-Natta catalyzed ethylene copolymer and a metallocene catalyzed ethylene copolymer fabricated as cast films have improved optical, toughness, heat sealability, film blocking and unwind noise properties when compared to metallocene catalyzed ethylene polymers alone. However, the improvements in tear and ultimate tensile are not shown to be balanced.

Similarly, Research Disclosure No. 37644 (Anonymous) teaches blends of Ziegler-Natta catalyzed resins and resins made using single site catalysis system exhibit superior TD tear resistance and superior MD ultimate tensile properties. Hodgson et al. in U.S. Patent No. 5,376,439 also describe film from a polymer blend which is said to have excellent elongation, tensile and impact properties.

WO 98/26000 discloses cast films prepared from interpolymer compositions comprising a substantially linear ethylene/α-olefin interpolymer and a heterogeneous interpolymer wherein the composition has an I_{10}/I_2 value of <10

This Sheet Has Been Replaced



and is characterized as having a log viscosity at 100 rad/s ≤ 4.43 - 0.8 x log(I_2) or a log relaxation time > -1.2 - 1.3 x log(I_2). The reported inventive examples have an average I_2 of 3.65 g/10 minutes and an average I_{10}/I_2 of 7.07 and range in M_w/M_n from 2.14 to 3.4 and in composition density from 0.9118 g/cm^3 to 0.9188 g/cm^3. The reported M_{v1}/M_{v2} ratios and TREF peak temperature differentials for inventive examples range from 0.577 to 0.728 and from 17 to 24°C, respectively. However, TREF peak temperature differentials are not shown to vary with composition density and no density differential between the component polymers or component molecular weights are reported in WO 98/26000, nor is any property balance or optical improvement discussed or reported.

Hence, in spite of the above disclosures, no known ethylene interpolymer composition exhibits high, balanced toughness, good processability and good optical properties. As such, there remains a need for an improved ethylene interpolymer composition, especially for use in blown film applications. There is also a need for a process for making an improved ethylene interpolymer composition with the desired property balance. There is also a need for a process for making an improved ethylene interpolymer composition wherein the process involves polymerization using multiple reactors and the process is characterized by improved flexibility such that a broad range of product molecular weights or densities (or a combination thereof) can be economically manufactured. There is also a need for a blown film with the desired property balance. These and other objects will become apparent from the detailed description of the present invention provided herein below.

We have discovered a multicomponent ethylene interpolymer composition which is characterized by a relatively narrow molecular weight distribution and a variably optimized compositional distribution with respect to its composition density and short chain branching

This Sheet Has Been Replaced
AS BEEN
ED

distribution or fractional component crystallinity. The broad aspect of the invention is a polymer composition comprising ethylene interpolymerized with at least one unsaturated comonomer, wherein the composition is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_2 in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities greater than or equal to 0.926 g/cm^3 and greater than 13°C at composition densities less than or equal to 0.92 g/cm^3.

A second aspect of the invention is a polymer composition comprising ethylene interpolymerized with at least one unsaturated comonomer, wherein the composition is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

b) an I_{10}/I_2 ratio greater than 6.6, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is in the range of from 0.6 to 1.2, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, is equal to or less than the product of the equation:

$$\Delta T = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5667.93$$

wherein ΔT is in degrees Celsius and ρ is composition density in g/cm^3.

In an especially preferred embodiment, the composition is further characterized as having:

(e) a ΔT which is in the range of from equal to or greater than the product of the equation:

$$\Delta T_{lower} = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5650.27$$

to equal to or less than the product of the equation:

$$\Delta T_{Upper} = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5667.93$$

where ΔT is in degrees Celsius and ρ is composition density in g/cm^3, and

(f) a density differential between the density of the second and first polymer component of less than or equal to 0.028 g/cm^3.

Another aspect of the invention is a process for making an ethylene polymer composition comprised of ethylene

This Sheet Has Been Replaced

interpolymerized with at least one unsaturated comonomer and characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_{10_2} in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities greater than or equal to 0.926 g/cm^3 and greater than 13°C at composition densities less than or equal to 0.92 g/cm^3,

the process comprising continuously operating at least two polymerization reactors.

The third aspect of the invention is a fabricated article comprising an ethylene interpolymer composition which comprises ethylene interpolymerized with at least one unsaturated comonomer and is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

b) an I_{10}/I_{2}, in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities greater than or equal to 0.926 g/cm^3 and greater than 13°C at composition densities less than or equal to 0.92 g/cm^3.

Brief Description of Drawings

FIG. 1 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Inventive Example 1 where ATREF-DV denotes analytical temperature rising elution fractionation coupled with a differential viscometer for viscosity average molecular weight determination as a function of elution temperature.

FIG. 2 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Inventive Example 2.

This Sheet Has Been Replaced

FIG. 3 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Comparative Example 3.

FIG. 4 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Comparative Example 4.

FIG. 5 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Comparative Example 5.

FIG. 6 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Inventive Example 6.

FIG. 7 is an ATREF-DV curve showing the short chain branching distribution as related to the viscosity-average molecular weight (M_v) for Comparative Example 7.

FIG. 8 is an ATREF curve showing the short chain branching distribution as for Comparative Example 8.

We have discovered that substantial distinctiveness between dominant polymer components of an ethylene interpolymer composition results in unbalanced, reduced toughness properties when the composition is converted into film form. In particular, we discovered that, surprisingly, a composition having a relatively narrow molecular weight distribution and comparatively high molecular weight can be manufactured with high, balanced toughness properties while maintaining good extrusion processability and optical properties providing its compositional distribution as determined by analytical temperature rising elution fractionation (ATREF) is appropriately optimized.

The term "ATREF peak temperature" as used herein refers to the elution temperature that corresponds to a peak observed on an ATREF curve as determined from temperature rising elution fractionation in the range of 20 to 110°C. A peak corresponds to a substantial weight percent of crystallized polymer portion based on the total amount of

This Sheet Has Been Replaced



crystallizable polymer portions for the whole composition. Every ethylene polymer composition with crystallizable polymer portions will have at least one ATREF peak temperature although the composition may be characterized as having measurable crystallized polymer portions at several different peak temperatures (that is, multiple peaks). For purposes of the present invention, an ATREF peak is discerned as distinguished from shoulders, humps and doublets. For example, in FIG. 1 and 2, Inventive Examples 1 and 2 are both shown to be characterized by only two ATREF peaks as the Log M_v response in FIG. 2 at about 90°C is not considered to constitute an ATREF peak. Similarly, the doublet shown in FIG. 4 for comparative example 4 is also considered to constitute a single ATREF peak. For the inventive composition, T_{peak1} will be the peak occurring at the lowest elution temperature and T_{peak2} will be the peak occurring at the highest elution temperature in the range of 20-110°C, although the composition may also have peaks at intermediate temperatures.

The term "composition density" as used herein means the density of a single component polymer or a polymer mixture of at least two ethylene polymers measured in accordance with ASTM D-792. The term "composition density" refers to a solid state density measurement of pellets, film or a molding as distinguished from a melt density determination.

The term "single polymer component" as used herein is distinct from the term "polymer fraction" which is used in the art in reference to a fractionated polymer. Thus, as used herein, a single polymer component comprises various polymer fractions and a polymer fraction comprises smaller polymer fractions(as can be shown using, for example, ATREF).

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 terms "homopolymer," "copolymer,"

This Sheet Has Been Replaced

"terpolymer" as well as "interpolymer."

The term "interpolymer", as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term "interpolymer" thus includes the term "copolymers" (which is usually employed to refer to polymers prepared from two different monomers) as well as the term "terpolymers" (which is usually employed to refer to polymers prepared from three different types of monomers).

The term "substantially linear ethylene polymer" is used herein to refer specially to homogeneously branched ethylene polymers that have long chain branching. The term does not refer to heterogeneously or homogeneously branched ethylene polymers that have a linear polymer backbone.

For substantially linear ethylene polymers, the long chain branches have the same comonomer distribution as the polymer backbone, and the long chain branches can be as long as about the same length as the length of the polymer backbone to which they are attached. The polymer backbone of substantially linear ethylene polymers is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons.

Long chain branching is defined herein as a chain length of at least 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The presence of long chain branching can be determined in ethylene homopolymers by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (Rev. Macromol. Chem. Phys., C29, V. 2&3, p. 285-297).

Although conventional ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms, there are other known

This Sheet Has Been Replaced



techniques useful for determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. Two such methods are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, for example, Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is a useful technique for quantifying the presence of long chain branches in substantially linear ethylene polymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using ^{13}C NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

DeGroot and Chum also showed that a plot of Log(I_2, melt index) as a function of Log(GPC Weight Average Molecular Weight) as determined by GPC-DV illustrates that the long

This Sheet Has Been Replaced

chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

For substantially linear ethylene polymers, the long chain branch is longer than the short chain branch that results from the incorporation of the α-olefin(s) into the polymer backbone. The empirical effect of the presence of long chain branching in the substantially linear ethylene polymers used in the invention is manifested as enhanced rheological properties which are quantified and expressed herein in terms of gas extrusion rheometry (GER) results or melt flow, I_{10}/I_2, increases (or a combination thereof).

The substantially linear ethylene polymers useful in this invention (homopolymers as well as interpolymers) surprisingly have excellent processability, even though they have relatively narrow molecular weight distributions. Substantially linear ethylene polymers have a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63.$$

Even more surprising, the melt flow ratio (I_{10}/I_2) of the substantially linear olefin polymers can be varied essentially independently of the polydispersity index (that is, molecular weight distribution (M_w/M_n)). This is contrasted with conventional heterogeneously branched linear polyethylene resins which have rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases. Also, for the substantially linear ethylene polymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, that is, the higher the I_{10}/I_2 ratio, the more long chain branching in the polymer.

This Sheet Has Been Replaced

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97-99. All GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15 x 10^6 dyne/cm^2. The substantially linear ethylene polymers described herein preferably have a PI in the range of 0.01 kpoise to 50 kpoise, preferably 15 kpoise or less. The substantially linear ethylene polymers described herein have a PI less than or equal to 70 percent of the PI of a comparative linear ethylene polymer which does not contain long chain branching but has about the same I_2 and M_w/M_n as the substantially linear ethylene polymer being compared.

An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymers is at least 50 percent greater than the critical

This Sheet Has Been Replaced



shear rate at the onset of surface melt fracture of a linear ethylene polymer which does not contain long chain branching but has about the same I_2 and M_w/M_n as the substantially linear ethylene polymer being compared, wherein "about the same" as used herein means that each value is within 10 percent of the comparative value of the comparative linear ethylene polymer.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

In addition to having a narrow molecular weight distribution, substantially linear ethylene polymers are characterized as having:

(a) melt flow ratio, $I_{10}/I_2 \geq 5.63$, and

(b) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer comprise the same comonomer or comonomers, the linear ethylene polymer has an I_2 and M_w/M_n within ten percent of the substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer.

This Sheet Has Been Replaced



Preferred substantially linear ethylene polymers are further characterized as having a single differential scanning calorimetry, DSC, melting peak between -30° and 150°C.

Substantially linear ethylene polymers are homogeneously branched ethylene polymers and are disclosed in U.S. Patent 5,272,236; U.S. Patent 5,278,272; and U.S. Patent No. 5,665,800. Homogeneously branched substantially linear ethylene polymers can be prepared via the continuous solution, slurry, or gas phase polymerization of ethylene and at least one optional α-olefin comonomer in the presence of a constrained geometry catalyst, such as the method disclosed in European Patent Application 416,815-A. The polymerization can generally be performed in any reactor system known in the art including, but not limited to, a tank reactor(s), a sphere reactor(s), a recycling loop reactor(s) or combinations thereof, any reactor or all reactors operated partially or completely adiabatically, nonadiabatically or a combination of both. Preferably, a continuous solution polymerization process is used to manufacture the substantially linear ethylene polymer used in the present invention.

The term "heterogeneously branched linear ethylene polymer" is used herein in the conventional sense in reference to a linear ethylene interpolymer having a comparatively low short chain branching distribution index. That is, the interpolymer has a relatively broad short chain branching distribution. Heterogeneously branched linear ethylene polymers have a SCBDI less than 50 percent and more typically less than 30 percent.

The term "homogeneously branched linear ethylene polymer" is used herein in the conventional sense to refer to a linear ethylene interpolymer in which the comonomer is randomly distributed within a given polymer molecule and wherein substantially all of the polymer molecules have the same ethylene to comonomer molar ratio. The term refers to

This Sheet Has Been Replaced



an ethylene interpolymer that is characterized by a relatively high short chain branching distribution index (SCBDI) or composition distribution branching index (CDBI). That is, the interpolymer has a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent. At higher degrees of compositional uniformity, homogeneously branched ethylene polymers can be further characterized as essentially lacking a measurable high density, high crystallinity polymer portion as determined using a temperature rising elution fractionation technique (abbreviated herein as "TREF").

Homogeneously branched ethylene polymers (that is, both substantially linear ethylene polymers and homogeneously branched linear ethylene polymers) for use in the present invention can be also described as having less than 15 weight percent, preferably less than or equal to 10 weight percent, more preferably less than or equal to 5 weight percent and most preferably zero (0) weight percent of the polymer with a degree of short chain branching less than or equal to 10 methyls/1000 carbons, preferably less than or equal to 5 methyls/1000 carbons. That is, the polymer contains no measurable high density polymer fraction (for example, there is no fraction having a density of equal to or greater than 0.94 g/cm^3), as determined, for example, using a temperature rising elution fractionation (TREF) technique and infrared or ^{13}C nuclear magnetic resonance (NMR) analysis. Conversely, heterogeneously branched ethylene polymers can be described as having greater than or equal to 15 weight percent (based on the total weight of the polymer) of the polymer with a degree of short chain branching less than or equal to 10 methyls/1000 carbons.

Preferably, the homogeneously branched ethylene polymer is characterized as having a narrow, essentially single melting TREF profile/curve and essentially lacking a measurable high density polymer portion, as determined using

This Sheet Has Been Replaced

a temperature rising elution fractionation technique (abbreviated herein as "TREF").

SCBDI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content and represents a comparison of the monomer distribution in the interpolymer to the monomer distribution expected for a Bernoullian distribution. The SCBDI of an interpolymer can be readily calculated from TREF as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent 4,798,081; 5,008,204; or by L. D. Cady, "The Role of Comonomer Type and Distribution in LLDPE Product Performance," SPE Regional Technical Conference, Quaker Square Hilton, Akron, Ohio, October 1-2, pp. 107-119 (1985). However, the preferred TREF technique does not include purge quantities in SCBDI calculations. More preferably, the monomer distribution of the interpolymer and SCBDI are determined using ^{13}C NMR analysis in accordance with techniques described in US Patent No. 5,292,845; US Patent No. 4,798,081; U.S. Patent No. 5,089,321 and by J. C. Randall, Rev. Macromol. Chem. Phys., C29, pp. 201-317.

In analytical temperature rising elution fractionation analysis (as described in US Patent No. 4,798,081 and abbreviated herein as "ATREF"), the film or composition to be analyzed is dissolved in a suitable hot solvent (for example, trichlorobenzene) and allowed to crystallized in a column containing an inert support (stainless steel shot) by slowly reducing the temperature. The column is equipped with both a refractive index detector and a differential viscometer (DV) detector. An ATREF-DV chromatogram curve is then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the eluting solvent (trichlorobenzene). The ATREF curve is also frequently called the short chain branching distribution (SCBD), since it indicates how evenly the comonomer (for example, octene) is distributed throughout the sample in that as elution

This Sheet Has Been Replaced EEN

temperature decreases, comonomer content increases. The refractive index detector provides the short chain distribution information and the differential viscometer detector provides an estimate of the viscosity average molecular weight. The short chain branching distribution and other compositional information can also be determined using crystallization analysis fractionation such as the CRYSTAF fractionalysis package available commercially from PolymerChar, Valencia, Spain.

The inventive composition is broadly characterized as having a M_{v1}/M_{v2} in the range of from 0.6 to 1.2, preferably less than or equal to 1.0 and more preferably in the range of from 0.8 to 1. When M_{v1}/M_{v2} is substantially diverge from 1.0, compositions with improved dart impact resistance may result, however, other toughness properties (that is, ultimate tensile strength and tear resistance) will invariably be unbalanced when fabricated as blown film.

The inventive composition at a composition density of in the range of from 0.92 g/cm^3 to 0.926 g/cm^3 is characterized as having an ATREF peak temperature differential with respect to the at least two component polymers in the range of 10°C to 22°C, preferably from 12°C to 20°C and more preferably from 14°C to 18°C. However, persons skilled in the art having appreciated the present invention, especially the Examples reported herein below, will recognize that the distinguishing ΔT parameter of the present invention varies with composition densities. Accordingly, the inventive composition is generally characterized as having a ΔT which decreases with increased composition density such that ΔT is less than 23°C at composition densities greater than or equal to 0.926 g/cm^3 and greater than 13°C at composition densities less than or equal to 0.92 g/cm^3. Preferably, however, the inventive composition is characterized as having a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2},

This Sheet Has Been Replaced



corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, is equal to or less than the product of the equation:

$$\Delta T = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5667.93$$

where ΔT is in degrees Celsius and ρ is composition density in g/ cm^3 and is especially characterized as having a ΔT which is equal to or greater than the product of the equation:

$$\Delta T_{lower} = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5650.27$$

and which is equal to or less than the product of the equation:

$$\Delta T_{Upper} = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5667.93$$

where ΔT is in degrees Celsius and ρ is composition density in g/cm^3. That is, the ΔT is in the range of the ΔT_{Lower} and ΔT_{upper}.

Preferably, the inventive composition is further characterized as having a density differential between the densities of the second and first polymer components in the range of from 0 to 0.028 g/cm^3, preferably in the range of from 0.008 to 0.026 g/cm^3, and more preferably from 0.01 to 0.016 g/cm^3.

Preferably, the inventive composition is further characterized as having a M_{w1}/M_{w2} (that is, a ratio of the weight average molecular weight of the first component polymer to the weight average molecular weight of the second component polymer, as determined by GPC which is independent of M_{v1}/M_{v2}) of less than or equal to 1.2, and preferably less than or equal to 1.

The composition density of the novel composition is generally less than 0.945 g/cc, preferably less than 0.94 g/cc and more preferably less than 0.938 g/cc, and is

This Sheet Has Been Replaced



especially in the range of from 0.90 to 0.945 g/cm^3, more especially in the range of from 0.912 to 0.938 g/cm^3 and most especially in the range of from a0.915 to 0.935 g/cm^3 (as measured in accordance with ASTM D-792).

The molecular weight of polyolefin polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The overall I_2 melt index of the novel composition is preferably in the range of from 0.001 to 200 g/10 minutes, more preferably from 0.01 to 20 g/10 minutes, most preferably from 0.01 to 10 g/10 minutes and especially when fabricated as blown films is in the range from 0.1 to 2.2 g/10 minutes, more preferably from 0.2 and 1.8 g/10 minutes.

Other measurements useful in characterizing the molecular weight of ethylene interpolymer compositions involve melt index determinations with higher weights, such as, for common example, ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition N" and also known as I_{10}). The ratio of a higher weight melt index determination to a lower weight determination is known as a melt flow ratio, and for measured I_{10} and the I_2 melt index values the melt flow ratio is conveniently designated as I_{10}/I_2.

Broadly, the inventive composition has an I_{10}/I_2 melt flow ratio greater than 6.6, more preferably greater than or equal to 6.9, most preferably greater than or equal to 7.1, and especially in the range of from greater than 6.6 to 8.2 , more especially in the range of from 6.7 to 8.2 and most especially in the range of from 6.8 to 7.8.

However, in certain preferred embodiments, where maximized optical properties and improved processability are desired, at least one polymer component will be a

This Sheet Has Been Replaced



EN

substantially linear ethylene polymer (that is, an ethylene polymer made in a continuous polymerization process using a constrained geometry catalyst system and which results in the so-made polymer having long chain branching). In such preferred embodiments, the inventive composition itself is preferably further characterized as having (in the range of from 0.01 long chain branches/1,000 carbons to 3 long chain branches/1,000 carbons) greater than or equal to 0.08 long chain branch per 10,000 carbons, more preferably greater than or equal to 0.1 long chain branch per 10,000 carbons and most preferably greater than or equal to 0.2 long chain branch per 10,000 carbons.

The molecular weight distributions of ethylene polymers are determined by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with a differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of 10^3, 10^4, 10^5 and 10^6Å. The solvent is 1,2,4-trichlorobenzene, from which about 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is about 1.0 milliliters/minute, unit operating temperature is about 140°C and the injection size is about 100 microliters.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968) to derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^b.$$

In this equation, a = 0.4316 and b = 1.0. Weight average molecular weight, M_w, is calculated in the usual manner

This Sheet Has Been Replaced

according to the following formula: $M_j = (\Sigma w_i(M_i^j))^j$; where w_i is the weight fraction of the molecules with molecular weight M_i eluting from the GPC column in fraction i and j = 1 when calculating M_w and j = -1 when calculating M_n. The novel composition has M_w/M_n less than or equal to 3.3, preferably less than or equal to 3, and especially in the range of from 2.4 to 3.

ATREF analysis can conveniently illuminate several key structural features of a film or composition. For example, homogeneously branched ethylene polymers such as AFFINITY resins supplied by The Dow Chemical Company, ENGAGE resins supplied by Dupont Dow Elastomers, TAFMER resins supplied by Mitsui Chemical Corporation and EXACT resins supplied by Exxon Chemical Corporation are known to exhibit a unique symmetrical single elution peak (or homogeneous SCBD). In contrast, ethylene polymers produced by a conventional Ziegler-Natta catalyst system (such as, for example, DOLWEX LLDPE resins supplied by The Dow Chemical Company) are known to exhibit a bimodal or heterogeneous SCBD with both a broad and a narrow peak eluting at significantly different temperatures.

Because the uniqueness of the shape of ATREF curves and elution temperatures correspond to polymer densities, ATREF analysis can be used to fingerprint particular polymers. In particular, for compositions consisting of multiple component polymers, by integrating the ATREF curve, the weight fraction of each component can be conveniently determined. Further, the density of component polymers can be determined from ATREF analysis where the composition is known from measurement in accordance with ASTM D-792. For example, for substantially linear ethylene polymers, calibration curves of ATREF elution temperature versus polymer density provide polymer density is defined by:

$$\rho = 0.83494 + 9.6133 \times 10^{-4}(T_e)$$

This Sheet Has Been Replaced
BEEN REPLACED

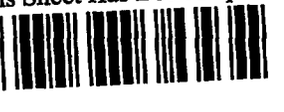
where T_e is the ATREF elution temperature of the polymer. Given the overall composition density of the composition, the weight fraction of the component polymer by integration of the ATREF curve and the polymer density of the substantially linear ethylene polymer component, the density of the remain component polymer can be conveniently calculated.

To further characterize a polymer composition or mixture, a differential viscometer may be employed. The output from a differential viscometer is the viscosity average molecular weight, M_v, which indicates the variation in molecular weight as a function of elution volume. The M_v response can indicate which component polymer is characterized as having a higher molecular weight or whether the component polymers are characterized as having substantially equivalent molecular weights.

In summary, given the ATREF curve and composition density of a film or composition, the weight fraction and polymer densities of the component polymers can be calculated. Combining ATREF analysis with a differential viscometer (ATREF/DV) gives an indication of the relative molecular weights of the component polymers. As such, AFTREF/DV can be used to fingerprint the film or composition of the present invention. The AFREF curve will show at least two distinct elution peaks given to density differential between the first and second ethylene polymers of the invention and preferred embodiments will exhibit a single elution peak associated with the first ethylene polymer component and a second ethylene polymer component having a higher molecular weight than the first ethylene polymer component.

A GPC deconvolution technique can be used to determine the melt index of individual ethylene polymer components. In this technique, GPC data are generated using a Waters 150C high temperature GPC chromatograph as described herein above. Given empirical elution volumes, molecular weights can be

This Sheet Has Been Replaced



conveniently calculated using a calibration curve generated from a series of narrow molecular weight distribution polystyrene standards. The GPC data should be normalized prior to running the deconvolution procedure to insure an area of unity under the weight fraction versus log(MW) GPC curve.

For the deconvolution technique, homogeneously branched ethylene polymers are assumed to follow a Bamford-Tompa molecular weight distribution, that is, Eq. [1],

$$w_i(M_i) = \ln(10)\frac{M_i}{M_n}\exp((-\frac{M_i(1+\zeta)}{M_n}))\times(\frac{2+\zeta}{\zeta})^{1/2}\times I_1(\frac{M_i\zeta^{1/2}(2+\zeta)^{1/2}}{M_n}) \qquad [1]$$

where w_i is the weight fraction of polymer with molecular weight M_i, M_n is the number average molecular weight, $I_1(x)$ is the modified Bessel function of the first kind of order one, defined by Eq.[2],

$$I_1(x) = \sum_b \frac{x^{2b+1}}{2^{2b+1}b!(b+1)!} \qquad [2]$$

and ζ is an adjustable parameter which broadens the molecular weight distribution, as shown in Eq.[3].

$$\frac{M_w}{M_n} = 2+\zeta \qquad [3]$$

For the deconvolution technique, heterogeneously branched ethylene polymers (that is, polymers manufactured using a Ziegler-Natta catalyst system) are assumed to follow a log-normal distribution, Eq.[4],

$$w_i(M_i) = \frac{1}{\beta(2\pi)^{0.5}}\exp(-\frac{1}{2}(\frac{\log(M_i)-\log(M_o)}{\beta})^2) \qquad [4]$$

where w_i is the weight fraction of polymer with molecular weight M_i, M_o is the peak molecular weight and β is a parameter which characterizes the width of the distribution. β was assumed to be a function of M_o, as shown in Eq. [5].

$$\beta = 5.70506 - 2.52383\,Log(M_o) + 0.30024(Log(M_o))^2 \qquad [5]$$

The GPC deconvolution technique involves a four parameter fit, M_n and ζ for a homogeneously branched ethylene

This Sheet Has Been Replaced

polymer (typically the first ethylene polymer component of the invention), M_o for a heterogeneously branched ethylene polymer (preferably the second component polymer of the invention) and the weight fraction amount of the homogeneously branched ethylene polymer. A non-linear curve-fitting subroutine within SigmaPlot™ supplied by Jandel Scientific (v3.03) is used to estimate these parameters. Given the number average molecular weight (M_n) , Eq.[3], of the homogeneously branched ethylene polymer or the first ethylene polymer component, its I_{10}/I_2 melt flow ratio and its density, its I_2 melt index can be conveniently calculated using Eq.[6].

$$I_2^{FCPA} = \exp(62.782 - 3.8620\,Ln(M_w) - 1.7095\,Ln((\frac{I_{10}}{I_2})^{FCPA}) - 16.310 \times \rho^{FCPA}) \qquad [6]$$

where FCPA denotes the ethylene polymer component.

The novel composition can be formed by any convenient method, including dry blending selected polymer components together and subsequently melt mixing the component polymers in an extruder or by mixing the polymer components together directly in a mixer (for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin screw extruder including a compounding extruder and a side-arm extruder employed directly down stream of a polymerization process).

Preferably, the novel composition is manufactured *in-situ* using any polymerization method and procedure known in the art (including solution, slurry or gas phase polymerization processes at high or low pressures) provided the operations, reactor configurations, and catalysis systems are selected, employed and carried out to indeed provide the novel composition with its defined combination of characteristics. A preferred method of manufacturing the novel composition involves the utilization of a multiple reactor polymerization system with the various reactors operated in series or in parallel configuration or a

This Sheet Has Been Replaced

combination of both where more than two reactors are employed. More preferably, the novel composition is manufactured using a two reactor system wherein the two reactors are operated in a series configuration.

The inventive composition preferably comprises greater than or equal to 40 weight percent of the first component polymer, more preferably greater than or equal to 45 weight percent of the first component polymer and preferably less than or equal to 60 weight percent of the second component polymer, more preferably less than or equal to 55 weight percent of the second component polymer, based on the total weight of the composition.

In one especially preferred embodiment of the present invention, the invention compositions comprises from 60 to 75 weight percent of the first component polymer and from 5 to 40 weight percent of the second component polymer, especially from 65 to 70 weight percent of the first component polymer and from 10 to 30 weight percent of the second component polymer, based on the total weight of the composition.

In a multiple reactor polymerization system (and especially in a two reactor system) with reactors configured in series, the polymer split is generally greater than or equal to 40 weight percent, preferably in the range of from 45 to 80 weight percent, more preferably in the range of from 60 weight percent to 75 weight percent, and most preferably in the range of from 65 to 70 weight percent for the first reactor in the series, based on total amount of polymer produced by the polymerization system.

Preferably, the first component (that is, the polymer component manufactured in the first reactor of a series) will be characterized by a lower polymer density and a molecular weight equal to or lower than the second (or last) component polymer (that is,. $M_{w1}/M_{w2} \leq 1$). To insure this preference, it may be necessary in a continuous polymerization system to adjust the percent of make-up comonomer feed (for example,

This Sheet Has Been Replaced

octene) to the second reactor (or any other reactor other than the first reactor in a series).

If the multiple reactor polymerization comprises two reactors, then the polymer mass split to the second reactor in the series will generally be equal to or less than 60 weight percent and preferably in the range of from 40 weight percent to 55 weight percent. The first reactor is a series configuration will typically be that reactor situated furthest away from the product outlet to finishing operations.

Also, in a preferred embodiment of the invention, a polymerization system consisting of at least one recirculating flow loop reactor and especially a polymerization system consisting of at least two recirculating loop reactors operated nonadiabatically (more especially with each loop reactor having heat exchange/removal capacities) is employed to manufacture the novel composition. Such preferred polymerization systems are as described by Kao et al. in WO 97/36942.

The nonadiabatic polymerization is preferably achieved at a continuous volumetric heat removal rate equal to or greater than 400 Btu/hour.cubic foot.°F (7.4 kW/m^3•°K), more preferably, equal to or greater than 600 Btu/hour.cubic foot.°F (11.1 kW/m^3•°K), more especially equal to or greater than 1,200 Btu/hour.cubic foot.°F (22.2 kW/m^3•°K) and most especially equal to or greater than 2,000 Btu/hour.cubic foot.°F (37 kW/m^3•°K).

"Volumetric heat removal rate" as used herein is the process heat transfer coefficient, U, in Btu/hour.square foot.°F, multiplied by the heat exchange area, A, in square feet, of the heat exchange apparatus divided by the total reactor system volume, in cubic feet. One of ordinary skill will recognize that there should be consistency respecting whether process side or outside parameters are used as to U and surface area calculations and determinations. The

This Sheet Has Been Replaced

calculations contained herein are based on outside surface areas and diameters of heat exchange tubes, coils, etc. whether or not the reactor mixture flows through such tubes, coils, etc. or not.

To effectuate nonadiabatic polymerization, any suitable heat exchange apparatus may be used, in any configuration, including, for example, a cooling coil positioned in a polymerization reactor or reactors, a shell-and-tube heat exchanger positioned in a polymerization reactor or reactors wherein the reactor flow stream(s) (also referred to in the art as "reaction mixture") passes through the tubes, or an entire recirculating flow loop reactor being designed as a heat exchange apparatus by providing cooling via a jacket or double piping. In a suitable design, a form of a shell-and-tube heat exchanger can be used wherein the exchanger housing has an inlet and an outlet for the reactor flow stream and an inlet and outlet for heat transfer media (for example, water, water/glycol, steam, SYLTHERMO™ material or media supplied by The Dow Chemical Company under the designation DOWTHERM®). In another design, the reactor flow stream flows through a plurality of heat transfer tubes within the heat exchanger housing while the heat transfer media flows over the tubes' exterior surfaces transferring the heat of reaction or polymerization from the reactor flow stream. Alternatively, the reaction stream flows through the housing and the heat transfer media flows through the tubes. Suitable heat exchange apparatuses for use in the manufacturing of the novel composition are commercially available items (such as, for example, a static mixer/heat exchanger supplied by Koch) having a tortuous path therethrough defined by the tubes' tubular walls or having solid static interior elements forming an interior web through which the reaction mixture flows (or a combination thereof).

The polymerization reaction to prepared the component polymers may be any reaction type or combination of reactions known in the art, including polymerization by solution, high

This Sheet Has Been Replaced
SHEET HAS BEEN REPLACED

pressure, slurry and gas pressure. In one preferred embodiment, polymerization is conducted under continuous slurry or solution polymerization conditions in at least one reactor to prepared at least one component polymer. In another embodiment, the polymerization is conducted under continuous solution polymerization conditions in at least one reactor to prepare the first component polymer. In another embodiment, the polymerization is conducted under continuous slurry polymerization conditions in at least one reactor to prepare the second component polymer.

It is generally contemplated that any known catalyst system useful for polymerizing olefins can be used to manufacture the novel composition including, for example, conventional Ziegler-Natta catalyst systems, chromium catalyst systems, so-called single site metallocene catalyst systems such as the monocyclo-pentadienyl transition metal olefin polymerization catalysts described by Canich in US Patent 5,026,798 or by Canich in US Patent 5,055,438 and constrained geometry catalyst systems as described by Stevens et al. in US Patent 5,064,802. However, in preferred embodiments, a metallocene catalyst system and conventional Ziegler-Natta catalyst system are used to manufacture the novel composition. For preferred embodiments that utilize a polymerization system consisting of at least two reactors in series configuration, preferably a constrained geometry catalyst system is employed in the first reactor (or first set of reactors) and a conventional Ziegler-Natta catalyst system is employed in the second reactor (or last set of reactors).

Catalysts and catalyst systems for use in the invention are described, for example, in EP-A-0 277 003; EP-A-0 277 004; EP-A-0 420 436; PCT International Publications WO 91/04257; WO 92/00333; WO 93/08221; and WO 93/08199, U.S. Pat. Nos. 3,645,992; 4,076,698; 4,612,300; 4,937,299; 5,096,867; 5,055,438; and 5,064,802.

This Sheet Has Been Replaced



:N

Suitable metallocene catalyst components for use in the present invention may be derivatives of any transition metal including Lanthanides, but preferably of Group 3, 4, or Lanthanide metals which are in the +2, +3, or +4 formal oxidation state. Preferred compounds include metal complexes containing from 1 to 3 π-bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized π-bonded anionic ligand groups. Exemplary of such π-bonded anionic ligand groups are conjugated or nonconjugated, cyclic or non-cyclic dienyl groups, allyl groups, and arene groups. By the term "π-bonded" is meant that the ligand group is bonded to the transition metal by means of a π bond.

Examples of suitable anionic, delocalized π-bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydro-fluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, and decahydro-anthracenyl groups, as well as C_1-C_{10} hydrocarbyl-substituted or C_1-C_{10} hydrocarbyl-substituted silyl substituted derivatives thereof. Preferred anionic delocalized π-bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetra-methylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydro-fluorenyl, octahydrofluorenyl, and tetrahydroindenyl.

Suitable cocatalysts for use herein include but are not limited to, for example, polymeric or oligomeric aluminoxanes, especially methyl aluminoxane or modified methyl aluminoxane (made, for example, as described in US Patent Nos.: 5,041,584; 4,544,762; 5,015,749; and 5,041,585 as well as inert, compatible, non-coordinating, ion forming compounds. Preferred cocatalysts are inert, non-coordinating, boron compounds.

The Ziegler catalysts suitable for the preparation of the heterogeneous component of the current invention are

This Sheet Has Been Replaced
BEEN

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. 4,314,912 (Lowery, Jr. et al.), 4,547,475 (Glass et al.), and 4,612,300 (Coleman, III).

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-hexylmagnesium, 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.

Among the halide sources which can be employed herein are the 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 wherein hydrocarbyl is as defined hereinbefore. By an active organic halide is meant a hydrocarbyl halide that contains a labile halogen at least as active, that is, as easily lost to another compound, as the halogen of sec-butyl chloride, preferably as active as t-butyl chloride. In addition to the

This Sheet Has Been Replaced

organic monohalides, it is understood that organic dihalides, trihalides and other polyhalides that are active as defined herein before 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, α-phenylethyl bromide, diphenyl methyl chloride. Most preferred are hydrogen chloride, *t*-butyl chloride, allyl chloride and benzyl chloride.

Suitable metallic halides which can be employed herein 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 as hereinbefore defined 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.

This Sheet Has Been Replaced



It is understood that the organic moieties of the aforementioned organomagnesium, for example, R", and the organic moieties of the halide source, for example, R and R', are suitably any other organic radical provided that they do not contain functional groups that poison conventional Ziegler catalysts.

The magnesium halide can be pre-formed from the organomagnesium compound and the halide source or it can be formed in situ in which instance the catalyst is preferably prepared by mixing in a suitable solvent or reaction medium (1) the organomagnesium component and (2) the halide source, followed by the other catalyst components.

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: $TrX'_{4-q}(OR^1)_q$, $TrX'_{4-q}R^2_q$, VOX'3 and VO $(OR^1)_3$.

wherein:

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

R^2 is an alkyl group, aryl group, aralkyl group, or substituted aralkyls.

The aryl, aralkyls and substituted aralkys contain 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms. When the transition metal compound contains a hydrocarbyl group, R^2, being an alkyl, cycloalkyl, aryl, or aralkyl group, the

This Sheet Has Been Replaced

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, neo-pentyl, 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 but non-limiting examples of the transition metal compounds include $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_8H_{17})_2Br_2$, and $Ti(OC_{12}H_{25})Cl_3$, $Ti(O\text{-}i\text{-}C_3H_7)_4$, and $Ti(O\text{-}n\text{-}C_4H_9)_4$.

Illustrative but non-limiting examples of vanadium compounds include VCl_4, $VOCl_3$, $VO(OC_2H_5)_3$, and $VO(OC_4H_9)_3$.

Illustrative but non-limiting examples of zirconium compounds include $ZrCl_4$, $ZrCl_3(OC_2H_5)$, $ZrCl_2(OC_2H_5)_2$, $ZrCl(OC_2H_5)_3$, $Zr(OC_2H_5)_4$, $ZrCl_3(OC_4H_9)$, $ZrCl_2(OC_4H_9)_2$, and $ZrCl(OC_4H_9)_3$.

As indicated above, mixtures of the transition metal compounds may be usefully employed, no restriction being imposed on the number of transition metal compounds which may be contracted with the support. Any halogenide and alkoxide transition metal compound or mixtures thereof can be usefully employed. The previously named transition metal compounds are especially preferred with vanadium tetrachloride, vanadium oxychloride, titanium tetraisopropoxide, titanium tetrabutoxide, and titanium tetrachloride being most preferred.

Suitable catalyst materials may also be derived from a inert oxide supports and transition metal compounds. Examples of such compositions suitable for use in the solution polymerization process are described in U.S. Pat No. 5,420,090 (Spencer. et al.), the teachings of which are incorporated herein by reference.

The inorganic oxide support used in the preparation of the catalyst may be any particulate oxide or mixed oxide as

This Sheet Has Been Replaced



previously described which has been thermally or chemically dehydrated such that it is substantially free of adsorbed moisture.

The specific particle size, surface area, pore volume, and number of surface hydroxyl groups characteristic of the inorganic oxide are not critical to its utility in the practice of the invention. However, since such characteristics determine the amount of inorganic oxide to be employed in preparing the catalyst compositions, as well as affecting the properties of polymers formed with the aid of the catalyst compositions, these characteristics must frequently be taken into consideration in choosing an inorganic oxide for use in a particular aspect of the invention. In general, optimum results are usually obtained by the use of inorganic oxides having an average particle size in the range of 1 to 100 microns, preferably 2 to 20 microns; a surface area of 50 to 1,000 square meters per gram, preferably 100 to 450 square meters per gram; and a pore volume of 0.5 to 3.5 cm^3 per gram; preferably 0.5 to 2 cm^3 per gram.

In order to further improve catalyst performance, surface modification of the support material may be desired. Surface modification is accomplished by specifically treating the support material such as silica, alumina or silica-alumina with an organometallic compound having hydrolytic character. More particularly, the surface modifying agents for the support materials comprise the organometallic compounds of the metals of Group IIA and IIIA of the Periodic Table. Most preferably the organometallic compounds are selected from magnesium and aluminum organometallics and especially from magnesium and aluminum alkyls or mixtures thereof represented by the formulas and R^1MgR^2 and $R^1R^2AlR^3$ wherein each of R^1, R^2 and R^3 which may be the same or different are alkyl groups, aryl groups, cycloalkyl groups, aralkyl groups, alkoxide groups, alkadienyl groups or alkenyl

This Sheet Has Been Replaced

groups. The hydrocarbon groups R^1, R^2 and R^3 can contain between 1 and 20 carbon atoms and preferably from 1 to 10 carbon atoms.

The surface modifying action is effected by adding the organometallic compound in a suitable solvent to a slurry of the support material. Contact of the organometallic compound in a suitable solvent and the support is maintained from 30 to 180 minutes and preferably from 60 to 90 minutes at a temperature in the range of 20° to 100°C. The diluent employed in slurrying the support can be any of the solvents employed in solubilizing the organometallic compound and is preferably the same.

Any convenient method and procedure known in the art can be used to prepare a Ziegler-Natta catalyst suitable for use in the present invention. One suitable method and procedure is described in U.S. Patent No. 4,612,300, in Example P. The described method and procedure involves sequentially adding to a volume of Isopar™ E hydrocarbon, a slurry of anhydrous magnesium chloride in Isopar™ E hydrocarbon, a solution of $EtAlCl_2$ in n-hexane, and a solution of $Ti(O\text{-}iPr)_4$ in Isopar™ E hydrocarbon, to yield a slurry containing a magnesium concentration of 0.166 M and a ratio of Mg/Al/Ti of 40.0:12.5:3.0. An aliquot of this slurry and a dilute solution of Et_3Al (TEA) are independently pumped in two separate streams and combined immediately prior to introduction polymerization reactor system to give an active catalyst with a final TEA:Ti molar ratio of 6.2:1.

More preferably, the support (e.g. silica and magnesium) to metal (e.g. vanadium, zirconium and titanium) molar ratio and the support surface area will be high. In one preferred embodiment, a $MgCl_2$ supported titanium catalyst system is employed to manufacture the second polymer component wherein the molar ratio between the magnesium and the titanium is in the range of 40 moles of Mg to less than 3 moles of Ti, preferably 40 moles of Mg to less than 2 moles Ti, more

This Sheet Has Been Replaced

preferably 40.0 moles of Mg to 1.3-1.7 moles of Ti. Most preferably, this $MgCl_2$ supported titanium catalyst system is characterized by the $MgCl_2$ having a single pore size distribution of 20 to 25 microns and a specific surface area of 400 to 430 m^2/gram.

Preferred dialkylmagnesium precursors for Mg support Ziegler Natta organomagnesium catalyst system are butyloctylmagnesium or butylethylmagnesium which are often stabilized with butykated hydroxytoluene (BHT) at about 0.5 mol%.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers, conjugated or non-conjugated dienes, polyenes, etc. Examples of such comonomers include C_3-C_{20} α-olefins such as propylene, isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, for example, cyclopentene, cyclohexene and cyclooctene. Thus, ethylene interpolymers within the purview of the present invention include, for example, but are not limited to, ethylene/propylene interpolymers, ethylene/1-butene interpolymers, ethylene/1-pentene interpolymers, ethylene/1-hexene interpolymers, ethylene/1-octene interpolymers and ethylene/styrene interpolymers.

Additives, such as antioxidants (for example, hindered phenolics, such as IRGANOX™ 1010 or IRGANOX™ 1076 supplied by Ciba Geigy), phosphites (for example, IRGAFOS™ 168 also supplied by Ciba Geigy), cling additives (for example, PIB), SANDOSTAB PEPQ™ (supplied by Sandoz), pigments, colorants, fillers, anti-stats, and processing aids may also be included

This Sheet Has Been Replaced

in the novel composition or fabricated article. Although generally not required, films, coatings and moldings formed from the novel composition may also contain additives to enhance antiblocking, mold release and coefficient of friction characteristics including, but not limited to, untreated and treated silicon dioxide, talc, calcium carbonate, and clay, as well as primary, secondary and substituted fatty acid amides, release agents, silicone coatings, etc. Still other additives, such as quaternary ammonium compounds alone or in combination with ethylene-acrylic acid (EAA) copolymers or other functional polymers, may also be added to enhance the antistatic characteristics of films, coatings and moldings formed from the novel composition and permit the use of the composition in, for example, the heavy-duty packaging of electronically sensitive goods.

The fabricated articles of the invention (such as, for example, but not limited to, a film, film layer, fiber, molding, sheet, pouch, bag, sack, tube and coating) may further include recycled and scrap materials and diluent polymers to provide, for example, multi-polymer blends to the extent that the desired property balanced is maintained. Exemplary diluent materials include, for example, elastomers (for example, EPDM, EPR, styrene butadiene block polymer such as styrene-isoprene-styrene, styrene-butadiene, styrene-butadiene-styrene, styrene-ethylene-styrene and styrene-propylene-styrene), natural and synthetic rubbers and anhydride modified polyethylenes (for example, polybutylene and maleic anhydride grafted LLDPE and HDPE), high density polyethylene (HDPE), medium density polyethylene (MDPE), heterogeneously branched ethylene polymers (for example, ultra or very low density polyethylene and linear low density polyethylene) and homogeneously branched ethylene polymers (for example, substantially linear ethylene polymers) as well as with high pressure polyethylenes such as, for example, low density polyethylene (LDPE), ethylene/acrylic acid (EAA)

This Sheet Has Been Replaced

interpolymers, ethylene/vinyl acetate (EVA) interpolymers and ethylene/methacrylate (EMA) interpolymers, and combinations thereof.

The fabricated article of the invention may find utility in a variety of applications. Suitable applications are thought to include, for example, but are not limited to, monolayer packaging films; multilayer packaging structures consisting of other materials such as, for example, biaxially oriented polypropylene or biaxially oriented ethylene polymer for shrink film and barrier shrink applications; packages formed via form/fill/seal machinery; peelable seal packaging structures; cook-in food packages; compression filled packages; heat seal films and packages for food packaging, snacks, grains, cereals, cheeses, frozen poultry and frozen produce; cast stretch films; monolayer shrink film; heat sealable stretch wrap packaging film; ice bags; foams; molded articles; bag-n-box; fresh cut produce packaging; fresh red meat retail packaging; liners and bags such as, for example, cereal liners, grocery/shopping bags, and especially heavy-duty shipping sacks and trash can liners (bags) where higher levels of downgauging are now possible due to the improved toughness properties exhibited by the fabricated article of the invention.

The fabricated article of the invention can be prepared by any convenient method known in the art. Suitable methods include, for example, lamination and coextrusion techniques or combinations thereof; blown film; cast film; extrusion coating; injection molding; blow molding; thermoforming; profile extrusion, pultrusion; calendering; roll milling; compression molding; rotomolding; injection blow molding; and fiber spinning and combinations thereof. Preferably, however, the novel composition is fabricated into a blown film for such uses as packaging, liner, bag or lamination applications, especially laminating films.

The fabricated article of the invention can be of any thickness required or desired for the intended end-use

This Sheet Has Been Replaced

BEEN

application. In particular, the novel film of the invention can be of any suitable film thickness, however, practitioners will appreciate the significant downgauging may be possible due to the high, balanced toughness properties of the novel film. For example, heavy duty shipping sacks typically have film thicknesses greater than 3 mils, especially greater than 7 mils.

Examples

The following examples are provided for the purpose of explanation and are not intended to limit the present invention in any way.

In an evaluation to investigate the comparative toughness and optical properties of various ethylene interpolymer compositions, several ethylene/1-octene copolymers were obtained. For this investigation, Inventive Examples 1, 2 and 6 and comparative examples 5 and 7 were manufactured using a non-adiabatic, continuous solution polymerization system consisting of two recirculating loop reactors configured in series. The process conditions employed in the manufacturing of Inventive Example 1 are provided in Table 1. Process conditions similar to those employed for Inventive Example 1 were also employed in the manufacture of Inventive Examples 2 and 6. The process conditions for comparative examples 5 and 7 were also similar to those employed for Inventive Example 1, except make-up comonomer was feed to the first loop reactor for the comparative examples. It is surprising that this process difference provides an optimized composition distribution for the inventive examples since the second reactor provides the higher density polymer component of the inventive examples. That is, the comonomer incorporation did not lower the polymer density as ordinarily expected, but instead provides an optimized compositional distribution that results in balanced toughness properties and improved optical properties.

This Sheet Has Been Replaced



Comparative examples 3, 4 and 8 were manufactured in a single recirculating loop reactor. For comparative examples 3 and 8, a conventional Ziegler-Natta catalyst system was employed under continuous solution polymerization conditions. Comparative example 4 was manufactured using a constrained geometry catalyst system according to methods and procedures described U.S. Patent 5,272,236; U.S. Patent 5,278,272; and U.S. Patent No. 5,665,800.

Table 1

	Inv. Ex 1	
	Flow Loop Rx1	Flow Loop Rx2
Process Temperature, °C	121	200
Process Pressure, psig (MPa)	535 (3.7)	535 (3.7)
Polymer Concentration wt. percent	16.6	21.9
C_2 Conversion, percent (overall)	77.5	86.1 (92.2)
Solvent/C_2 feed ratio	4.5	2.8
Solvent flow, lbs./hr (kg/hr)	653 (296)	316 (143)
C_2 flow, lbs./hr (kg/hr)	145 (66)	113 (51)
Make-up C_8 flow, lbs./hr (kg/hr)	0 (0)	24 (11)
Fresh Hydrogen flow, sccm	~1000	~2000
Feed Temp., °C	15	15
Recycle Ratio	17	10
Polymer split, weight percent	49.2	50.8
Residence time, min.	19	10
Catalyst Type	Constrained Geometry Catalyst system	Heterogeneous Ziegler-Natta Titanium coordination catalyst system
Catalyst efficiency, MM lbs. product/lb. Titanium (MM kg/kg)	2.0 (2.0)	0.3 (0.3)
Volumetric Heat Removal rate, BTU/hr*ft^3*°F (kW/m^3•°K)	400 (7.4)	630 (11.1)
Production rate, lbs./hr. (overall) ((kg/hr))	132 ((60))	137 ((62)) (269) (((122)))

Table 2 provides the physical properties of Inventive Examples 1 and 2 and comparative examples 3, 4 and 5.

This Sheet Has Been Replaced



Table 2

Property	Inv. Ex. 1	Inv. Ex. 2	Comp. Ex. 3†	Comp. Ex. 4†	Comp. Ex. 5†
Melt Index, I_2, g/10 min.	0.8	0.5	1.0	1.03	0.85
I_{10}/I_2	7.4	7.2	7.8	9.96	7.4
Composition Density, g/cc	0.921	0.921	0.920	0.918	0.920
GPC M_w	133,500	145,500	130,700	80,400	116,800
GPC M_n	47,100	49,700	34,300	38,467	34,900
M_w/M_n	2.83	2.93	3.81	2.09	3.35
ATREF T_{peak1}, °C	81.5	82	85	82.5	72
ATREF M_{v1}	94,400	118,900	100,000	97,724	158,500
ATREF T_{peak2}, °C	98	98	98	None	98
ATREF M_{v2}	158,500	167,900	149,600	NA	102,330
ATREF High Density Fraction, percent	14	22.2	15.9	0.5	20
M_{v1}/M_{v2}	0.60	0.71	0.67	NA	1.55
T_{peak2}-T_{peak1}, °C	16.5	16	13	NA	26
First Reactor Polymer Split, percent	49.2	51.8	NA	NA	36.8
*1st Reactor Polymer Density, g/cc	0.913	0.910	NA	NA	0.902
*1st Reactor Polymer I_2, g/10 min.	1.0	0.38	NA	NA	0.19
*1st Reactor Polymer M_w	97,400	127,900	NA	NA	158,300
*1st Reactor Polymer LCB/10000C	0.13	0.08	NA	NA	0.044
*2nd Reactor Polymer Density, g/cc	0.929	0.933	NA	NA	0.931
*2nd Reactor Polymer I_2, g/10 min.	0.4	0.6	NA	NA	2.4
*2nd Reactor Polymer M_w	149,700	135,900	NA	NA	92,635
1st M_w/2nd M_w	0.65	0.94	NA	NA	1.71
Density Differential (2nd-1st)	0.016	0.023	NA	NA	0.029

†Comparative example provided for purposes of comparison only; not an example of the present invention.
*Value predicted based on a kinetic model although a mass balance model would also suffice where direct measurement is not convenient.

This Sheet Has Been Replaced



Nominal 50 mm blown film was fabricated from Inventive Example 1 and 2 and comparative compositions 3, 4 and 5 on an Egan blown film unit equipped with 2 inch (5.1 cm) diameter, 32:1 L/D extruder and a 3 inch (7.6 cm) annular die. The blown film extrusion conditions for each example is provided in Table 3.

Table 3

Example	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3†	Comp. Ex 4†	Comp. Ex 5†
Die Gap, mils (mm)	35 (0.9)	35 (0.9)	35 (0.9)	35 (0.9)	35 (0.9)
Melt Temp., °F (°C)	453 (234)	462 (239)	450 (232)	450 (232)	450 (232)
Die Pressure, psi (MPa)	5,870 (40)	6,210 (43)	5,040 (35)	3,270 (23)	5,430 (37)
Output, lbs./hr. (kg/hr)	120 (54)	90 (41)	120 (54)	>120 (>54)*	120 (54)
Extruder Amperage	93	86	80	65	83
Blow-Up Ratio	2.7:1	2.7:1	2.7:1	2.7:1	2.7:1

†Comparative example provided for purposes of comparison only; not an example of the present invention.
*Value is an estimate, not an actual measurement.

During the actual blown film fabrication, all of the examples exhibited good bubble stability. However, surprisingly, although Inventive Examples 1 and 2 were characterized by substantially higher molecular weights and narrower molecular weight distributions relative to comparative example 3, the inventive examples exhibited comparable extrusion processibility; that is, the extrusion amperage for the inventive examples was only 8 to 16 percent higher than that for comparative example 3. This result is unexpected and surprising because typically narrower molecular weight distributions and higher molecular weights are both well-known to contribute to poor processability characteristics.

Table 4 lists film performance properties for Inventive Examples 1 and 2 and comparative examples 3, 4 and 5.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

Table 4

Example	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3†	Comp. Ex 4†	Comp. Ex 5†
Dart Impact (Method B), g	530	760	236	324	800
Elmendorf Type A - MD, g	570	538	691	526	510
Elmendorf Type A - CD, g	701	579	819	768	725
Elmendorf MD/CD	0.81	0.93	0.84	0.68	0.70
Ultimate Tensile - MD, psi (MPa)	7,340 (51)	8,189 (56)	6,525 (45)	6,787 (47)	6,700 (46)
Ultimate Tensile - CD, psi (MPa)	7,706 (53)	7,572 (52)	5,480 (38)	6,139 (42)	6,350 (44)
Ultimate Tensile MD/CD	0.95	1.08	1.19	1.11	1.06
Percent Film Haze	8.27	8.25	11.0	8.30	11.5

Elmendorf tear resistance was determined in accordance with ASTM D1922.
Ultimate tensile was determined in accordance with ASTM D638.
Percent film haze was determined in accordance with ASTM D1003.
†Comparative example provided for purposes of comparison only; not an example of the present invention.

Table 4 indicates that Inventive Examples 1 and 2 exhibited an excellent balance of performance properties. The inventive examples were characterized by balanced tear resistance, high and balanced ultimate tensile strength, high dart impact resistance and reduced film haze.

By "balanced tear resistance' it is meant that the ratio of MD tear to CD tear was in the range of from 0.8 to 1.

By "balanced ultimate tensile strength" it is meant that the ratio of MD ultimate tensile strength to CD ultimate tensile strength was in the range of from 0.9 to 1.1.

By "high dart impact resistance" it is meant that at a 0.908 g/cc density and 0.5 I_2, impact resistance would be ≥ 750 grams; at a 0.920 g/cc density and 0.5 I_2 ≥ 500 grams; and at a 0.926 g/cc density and 0.5 I_2 ≥ 250 grams. More particularly, since dart impact resistance is recognized to vary with density and melt index, high dart impact resistance was defined as a dart impact resistance (as determined in accordance with Method B) equal to or greater than the product of the equation:

$$\text{dart impact resistance} = 2181621.3 \times \text{den} - 1203704.2 \times \text{den}^2 - 273.7 \times \text{Log}I_2 - 987852.9$$

This Sheet Has Been Replaced

where den was composition density (in g/cm^3); den^2 was composition density squared and I_2 was melt index in accordance with ASTM D-1238, Condition 190°C/2.16 kg.

Surprisingly, the inventive examples exhibited reduced film haze even though they were characterized by higher molecular weight and larger ATREF temperature differential than comparative example 3. Even more surprisingly, Table 3 indicates that the film haze of the inventive examples was unexpectedly equivalent to comparative example 4 which was a homogeneously branched substantially linear ethylene polymer characterized by a more uniform compositional distribution, no high density polymer fraction, lower molecular weight and narrower molecular weight distribution, which are characteristics that are well-known to confer to improved optical properties.

In a second evaluation, polymer compositions having a nominal 0.926 g/cc composition density were compared. Table 5 shows the physical properties of the polymer compositions (Inventive Example 6 and comparative examples 7 and 8).

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

Table 5

Property	Inv. Ex. 6	Comp. Ex. 7†	Comp. Ex. 8†
Melt Index, I_2, g/10 min.	0.5	0.85	1.04
I_{10}/I_2	7.2	7.4	8.06
Composition Density, g/cc	0.926	0.926	0.9278
GPC M_w	147,900	119,900	115,000‡
GPC M_n	52,100	35,900	31,080‡
M_w/M_n	2.84	3.34	3.7
ATREF T_{peak1}, °C	87.5	75	87.5
ATREF M_{v1}	118,900	149,600	100,000‡
ATREF T_{peak2}, °C	98	98	97
ATREF M_{v2}	166,000	100,00	150,000‡
ATREF High Density Fraction, percent	27.1	45.9	25.0
M_{v1}/M_{v2}	0.72	1.5	0.67
$T_{peak2}-T_{peak1}$, °C	10.5	23	9.5
First Reactor Polymer Split, percent	50.7	39.5	NA
*1st Reactor Polymer Density, g/cc	0.918	0.906	NA
*1st Reactor Polymer I_2, g/10 min.	0.35	0.17	NA
*1st Reactor Polymer M_w	126,700	161,200	NA
*1st Reactor Polymer LCB/10000C	0.09	0.076	NA
*2nd Reactor Polymer Density, g/cc	0.934	0.939	NA
*2d Reactor Polymer I_2, g/10 min.	0.6	2.3	NA
*2nd Reactor Polymer M_w	133,400	92,936	NA
1st M_w/2nd M_w	0.95	1.73	NA
Density Differential (2nd-1st)	0.016	0.033	NA

†Comparative example provided for purposes of comparison only; not an example of the present invention.

*Value predicted based on a kinetic model. ‡Typical value.

This Sheet Has Been Replaced



Nominal 50 mm blown film was fabricated from Inventive Example 1 and 2 and comparative compositions 3, 4 and 5 on an Egan blown film unit equipped with 2 inch (5.1 cm) diameter, 32:1 L/D extruder and a 3 inch (7.6 cm) annular die. The blown film extrusion conditions employed for each example is provided in Table 6.

Table 6

Example	Inv. Ex 6	Comp. Ex 7†	Comp. Ex 8†
Die Gap, mils (mm)	35 (0.9)	35 (0.9)	35 (0.9)
Melt Temp., °F (°C)	460 (238)	468 (242)	462 (239)
Die Pressure, psi (MPa)	6,280 (43)	6,170 (43)	5,160 (36)
Output, lbs./hr. (kg/hr)	90 (41)	120 (54)	120 (54)
Extruder Amperage	85	81	71
Blow-Up Ratio	2.7:1	2.7:1	2.7:1

†Comparative example provided for purposes of comparison only; not an example of the present invention.

During the actual blown film fabrication, all of the examples exhibited good bubble stability. Table 7 lists film performance properties for Inventive Example 6 and comparative examples 7 and 8. Surprisingly, during blown film fabrication, Inventive Example 6 exhibited fair processability (nominal amperage) even though the novel composition was characterized by a substantially higher molecular weight and a narrower molecular weight distribution relative to comparative examples 7 and 8.

Table 7

Example	Inv. Ex 6	Comp. Ex 7†	Comp. Ex 8†
Dart Impact (Method B), g	250	410	177
Elmendorf Type A - MD	570	456	477
Elmendorf Type A - CD	627	803	718
Elmendorf MD/CD	0.91	0.57	0.66
Ultimate Tensile - MD, psi	6,785	6,820	6,975
Ultimate Tensile - CD, psi	6,856	7,006	4,800
Ultimate Tensile MD/CD	0.99	0.97	1.45
Percent Film Haze	10.27	14.0	12.0

Elmendorf tear resistance was determined in accordance with ASTM D1922.
Ultimate tensile was determined in accordance with ASTM D638.
Percent film haze was determined in accordance with ASTM D1003.
†Comparative example provided for purposes of comparison only; not an example of the present invention.

This Sheet Has Been Replaced
S BEEN
D

Table 7 indicates that Inventive Example 6 exhibited an excellent property balance. Relative to both comparative example 7 and 8, Inventive Example 6 exhibited superior tear resistance balance (cf. 0.91 versus 0.66 and 0.57). Also, the inventive example had superior tensile strength balance relative to comparative example 8 which was a heterogeneously branched ethylene/1-octene copolymer manufactured as described above with a Ziegler-Natta catalyst system.

Additionally, similar to the results shown for Inventive Examples 1 and 2, Table 7 indicates that Inventive Example 6 also exhibited surprisingly improved optical properties. The percent film haze of Inventive Example 6 was lower that the comparative examples 7 and 8 even though the inventive example possessed a substantially higher molecular weight as indicated by I_2 melt index values.

In another evaluation designed to further investigate the requirements for improved processability, good optical properties and improved toughness, several inventive examples and comparative examples were prepared. Table 8 provides the physical properties for the various polymer compositions which all have a nominal 0.921 g/cm^3 composition density.

Inventive Examples 9 and 10 and comparative examples 11 and 12 were all prepared using a process system and conditions similar to Inventive Example 1 (that is, a constrained geometry catalyst system was feed to the first reactor of a two-reactor polymerization system and a conventional Ziegler catalyst system was feed to the second reactor). Comparative example 13 was made in a single reactor polymerization system under continuous solution polymerization conditions using a MgCl supported Titanium Ziegler-Natta catalyst system having a high Mg:Ti molar ratio and a high Mg surface area.

Table 9 provides the performance properties for the Inventive Examples 9 and 10 and comparative examples 11-13 as

This Sheet Has Been Replaced

Table 8

Property	Inv. Ex 9	Inv. Ex 10	Comp. Ex 11†	Comp. Ex 12†	Comp. Ex 13†
Melt index, I_2, g/10 min.	0.87	0.76	0.83	0.8	1.02
I_{10}/I_2	7.6	6.9	8.1	8.8	7.6
Composition Density, g/cc	0.9204	0.921	0.9219	0.9221	0.9201
GPC Mw	125,000	123,000	132,300	115,600	125,400
GPC Mn	49,400	44,600	35,400	23,000	35,800
Mw/Mn	2.53	2.76	3.74	5.03	3.50
ATREF $Tpeak_1$, C	86	86	86	89	85
ATREF M_{v1}	89,500	99,900	137,000	191,000	89,900
ATREF $Tpeak_2$, C	99	99	99	99	98
ATREF M_{v2}	104,000	101,000	59,000	89,300	129,000
ATREF High Density Fraction, percent	15.3	15.5	9.4	8.4	12.4
M_{v1}/M_{v2}	0.86	0.99	2.32	2.14	0.70
$Tpeak_2$ - $Tpeak_1$, °C	13	13	13	10	13
First Reactor Polymer Split, percent	51	50	56	52	NA
*1st Reactor Polymer Density, g/cc	0.913	0.913	0.913	0.910	NA
*1st Reactor Polymer I_2, g/10 min.	0.6	0.4	0.2	0.2	NA
*1st Reactor Polymer Mw	112,100	125,500	143,400	149,300	NA
*1st Reactor Polymer LCB/10,000 C	0.20	0.09	0.08	0.09	NA
*2nd Reactor Polymer Density, g/cc	0.928	0.929	0.934	0.935	NA
*2nd Reactor Polymer I_2, g/10 min.	0.9	1.3	25	21	NA
*2nd Reactor Polymer Mw	120,100	109,000	48,900	51,300	NA
1st Mw/2nd Mw	0.93	1.15	2.93	2.91	NA
Density Differential (2nd - 1st)	0.015	0.015	0.021	0.025	NA

†Comparative example provided for purposes of comparison only; not an example of the present invention.

*Value predicted based on a kinetic model.

This Sheet Has Been Replaced

Table 9

Property	Inv. Ex 1	In. Ex 9	Inv. Ex 10	Comp. Ex 11†	Comp. Ex 12†	Comp. Ex 13†	Comp. Ex 3†	Comp. Ex 5†
Melt Index, I_2, (g/10 min.)	0.80	0.84	0.76	0.83	0.80	1.02	0.95	0.86
Composition Density (g/cc)	0.921	0.920	0.921	0.922	0.922	0.920	0.920	0.920
I_{10}/I_2	7.48	7.53	6.90	8.09	8.81	7.58	7.90	7.57
M_w/M_n	2.94	2.53	2.76	5.10	5.03	3.50	3.87	3.34
Vicat Softening Point (°C)	107.5	108.0	108.8	106.7	104.7	104.2	105.1	105.8
Extruder Amps	94	88	94	76	66	78	80	86
Extruder Die Pressure, psi (MPa)	6150 (42)	5780 (40)	6030 (42)	4860 (33)	4230 (29)	4600 (32)	4840 (33)	5320 (37)
Avg Haze Value, percent	7.4	7.6	7.3	11.6	13.7	7.9	10.8	10.5
DART (Method B), grams	544	472	550	452	250	274	266	646
Avg Elmendorf Type A CD, gms	806	909	802	758	765	702	885	862
Avg Elmendorf Type A MD, gms	550	544	562	480	512	883	626	467
Type A MD/CD	0.68	0.60	0.70	0.63	0.67	1.26	0.71	0.54
Avg Elmendorf Type B CD, gms	1102	1139	1056	1091	1235	1165	1082	960
Avg Elmendorf Type B MD, gms	754	718	747	674	667	877	781	598
Type B MD/CD	0.68	0.63	0.71	0.62	0.54	0.75	0.72	0.62
CD-Avg Ultimate Tensiles, psi (MPa)	5885 (41)	6550 (45)	6630 (46)	6191 (43)	5013 (35)	5657 (39)	4978 (34)	5810 (40)
MD-Avg Ultimate Tensiles, psi (MPa)	6383 (44)	7223 (50)	6791 (47)	6872 (47)	5972 (41)	7207 (50)	6289 (43)	7065 (49)
Ultimate Tensiles MD/CD	1.08	1.10	1.02	1.11	1.19	1.27	1.26	1.22
HSIT, °C	~101	~102	~101	~105	~110	~101	~100	~100
HTIT, °C	~102	~103	~102	~110	~116	~103	~101	~101

Note: 2 mil blown film. HSIT denotes heat seal initiation temperature. HTIT denotes hot tack initiation temperature.

†Comparative example provided for purposes of comparison only; not an example of the present invention.

This Sheet Has Been Replaced

The data in Table 9 indicates that Inventive Example 9 exhibits improved processability with improved optical properties while maintaining a high dart impact resistance. Comparative examples 11 and 12 which were two-component (polymer) compositions showed improved processability; however, their optical properties were objection and their sealing properties were poor (that is, the examples were characterized as having initiation temperatures which were higher than their Vicat Softening Point temperatures) rendering them inferior choices for use in, for example, laminating film applications.

In another evaluation, compositions with densities in the range of from 0.91 to 0.918 g/cm^3 were investigated. Table 10 provides the physical properties for these compositions.

Inventive Example 14 and comparative examples 17-20 were all made using a process system and conditions similar to Inventive Example 1. Comparative examples 17-20 were cast film compositions made in accordance with the teachings in WO 97/26000. Comparative examples 15 and 16 were both made in a single reactor polymerization system under continuous solution polymerization conditions. Comparative example 15 was made using a conventional TiCl Ziegler Natta catalyst system and comparative example 16 was made using a constrained geometry catalyst system as described in U.S. Patent 5,272,236; 5,278, 272; and 5,665,800.

Table 11 provides the performance properties for three of the compositions, Inventive Example 14 and comparative examples 15 and 16. Table 11 shows that relative to comparative example 16, Inventive Example 14 exhibits improved toughness balance with good optical properties and heat sealability. Relative to comparative example 15, Table 11 also shows that Inventive Example 14 exhibits comparable property balance with significantly improved impact resistance, optics and heat sealability. Further, it is contemplated that the processability of the Inventive Example

This Sheet Has Been Replaced



14 can be efficiently improved by increasing its long chain branching content while maintaining its other key improvement as exemplified or embodied, for example, in Inventive Example 9.

Table 10

Property	Inv. Ex 14	Comp. Ex 15†	Comp. Ex 16†	Comp. Ex 17†	Comp. Ex 18†	Comp. Ex 19†	Comp. Ex 20†
Melt index, I_2, g/10 min.	0.86	0.97	0.96	2.3	5	3.5	4
I_{10}/I_2	7.1	8.2	10.4	6.6	6.6	6.6	6.6
Composition Density, g/cc	0.9101	0.9126	0.9104	0.917	0.918	0.915	0.916
GPC Mw	120,600	116,600	86,100	95,900	75,600	81,400	ND
GPC Mn	43,500	31,200	38,000	37,700	27,700	33,600	ND
Mw/Mn	2.77	3.74	2.27	2.54	2.73	2.42	<3.3**
ATREF T_{peak1}, °C	74	76.5	78	78	79	76	75
ATREF M_{v1}	109,000	74,500	65,800	78,300	86,900	64,400	53,700
ATREF T_{peak2}, °C	99	99	None	99	99	99	99
ATREF M_{v2}	142,000	140,000	NA	109,000	86,100	98,600	69,200
ATREF High Density Fraction, percent	10.7	10.6	0	14.7	10.3	12.6	12.2
M_{v1}/M_{v2}	0.77	0.53	NA	0.72	1.01	0.65	0.78
$T_{peak2} - T_{peak1}$, °C	25	22.5	NA	21	20	23	24
First Reactor Polymer Split, percent	51	NA	NA	51	51	51	51
*1st Reactor Polymer Density, g/cc	0.900	NA	NA	0.911	0.912	0.909	0.9096
*1st Reactor Polymer I_2, g/10 min.	0.3	NA	NA	1	2.2	1.8	1.9
*1st Reactor Polymer M_W	141,400	NA	NA	98,600	80,600	86,100	ND
*1st Reactor Polymer LCB/10,000 C	0.05		NA	0.077	0.077	0.077	ND
*2nd Reactor Polymer Density, g/cc	0.921	NA	NA	0.923	0.924	0.921	0.9225
*2nd Reactor Polymer I_2, g/10 min.	5	NA	NA	2.9	6.5	4	5
*2nd Reactor Polymer M_W	76,000	NA	NA	87,900	70,400	80,300	ND
1st M_W/2nd M_W	1.86	NA	NA	1.12	1.14	1.07	ND
Density Differential (2nd - 1st)	0.021	NA	NA	0.012	0.012	0.012	0.0129

†Comparative example provided for purposes of comparison only; not an example of the present invention.
*Value predicted based on a kinetic model.
**Value is an estimate, not an actual measurement.

This Sheet Has Been Replaced
REPLACED

Table 11

Performance Properties	Inv. Ex 14	Comp. Ex 15†	Comp. Ex 16†
Melt Index, I_2, (g/10 min)	0.86	0.97	0.96
Composition Density (g/cc)	0.910	0.913	0.910
I_{10}/I_2	7.08	8.16	10.35
Vicat Soft. Pt. (°C)	94.7	94.1	96.7
Extruder Amps	97	75	73
Extruder Die Pressure, psi (MPa)	5360 (37)	4430 (31)	3820 (26)
Avg Haze Value, percent	3.8	7.1	2.4
Dart B, g	>850	610	>850
Modified Dart, g	>1470	776	1297
Avg Elmendorf Type A CD, g	822	904	685
Avg Elmendorf Type A MD, g	621	715	408
Type A MD/CD	0.75	0.79	0.60
Avg Elmendorf Type B CD, g	858	992	821
Avg Elmendorf Type B MD, g	621	862	477
Type B MD/CD	0.72	0.87	0.58
CD-Avg Ultimate Tensiles, psi (MPa)	8163 (56)	6322 (44)	ND
MD-Avg Ultimate Tensiles, psi (MPa)	6676 (46)	4731 (33)	ND
Ultimate Tensiles MD/CD	0.82	0.75	ND
HSIT, °C	~82-83	~92-93	~82-83
HTIT, °C	~90	~110	~93

Note: 2 mil blown film. HSIT denotes heat seal initiation temperature.
HTIT denotes hot tack initiation temperature.
†Comparative example provided for purposes of comparison only; not an example of the present invention.

In another evaluation, compositions with densities in the range of from 0.929 to 0.941 g/cm^3 were investigated. Table 12 provides the physical properties for these compositions and Table 13 provides the performance properties for the compositions. Inventive Examples 22-24 and comparative example 27 were all made using a process system and polymerization conditions similar to the employed for Inventive Example 1. Comparative examples 25 and 26 were made using a single reactor system under continuous solution polymerization conditions. Comparative example 25 was made using a conventional $MgCl_2Ti$ Ziegler Natta catalyst system. Comparative example 26 was made using a MgCl supported titanium Ziegler-Natta catalyst system having a high Mg:Ti molar ratio and a high Mg surface area.

This Sheet Has Been Replaced

EEN

Table 12

Property	Inv. Ex 22	Inv. Ex 23	Comp. Ex 24	Comp. Ex 25	Comp. Ex 26	Comp. Ex 27
Melt index, I_2, g/10 min.	0.79	0.94	0.67	1.03	0.81	2.3
I_{10}/I_2	7.5	7.1	8.2	7.8	8.2	7.4
Composition Density, g/cc	0.9295	0.9305	0.9328	0.9304	0.9305	0.9409
GPC M_W	125,100	128,100	127,600	120,200	116,300	92,100
GPC M_n	46,700	43,000	25,800	33,100	27,400	35,100
M_W/M_n	2.68	2.98	4.95	3.63	4.24	2.62
ATREF T_{peak1}, °C	90	94	94	92	94	89
ATREF M_{V1}	86,400	144,000	141,000	120,000	91,100	79,400
ATREF T_{peak2}, °C	99	None	None	97	98	100
ATREF M_{V2}	97,000	NA	NA	157,000	110,000	75,700
ATREF High Density Fraction, percent	81.3	79.7	75.6	70.7	65.8	60.3
M_{V1}/M_{V2}	0.89	NA	NA	0.76	0.83	1.05
$T_{peak2} - T_{peak1}$, °C	9	NA	NA	5	4	11
First Reactor Polymer Split, percent	49	53	59	NA	NA	29
*1st Reactor Polymer Density, g/cc	0.923	0.928	0.925	NA	NA	0.924
*1st Reactor Polymer I_2, g/10 min.	0.5	0.5	0.25	NA	NA	0.8
*1st Reactor Polymer M_W	111,300	109,800	134,000	NA	NA	96,300
*1st Reactor Polymer LCB/10,000 C	0.53	0.17	0.15	NA	NA	0.47
*2nd Reactor Polymer Density, g/cc	0.936	0.934	0.945	NA	NA	0.948
*2nd Reactor Polymer I_2, g/10 min.	0.9	1.3	60	NA	NA	2.6
*2nd Reactor Polymer M_W	120,000	108,200	38,500	NA	NA	90,000
1st M_W/2nd M_W	0.93	1.01	3.48	NA	NA	1.07
Density Differential (2nd - 1st)	0.014	0.006	0.020	NA	NA	0.025

†Comparative example provided for purposes of comparison only; not an example of the present invention.
*Value predicted based on a kinetic model.
**Value is an estimate, not an actual measurement.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

Table 13

Performance Properties	Inv. Ex 22	Inv. Ex 23	Comp. Ex 24†	Comp. Ex 25†
Melt Index, I_2, (g/10 min.)	0.79	0.94	0.67	1.03
Composition Density (g/cc)	0.929	0.931	0.933	0.930
I_{10}/I_2	7.45	7.07	8.15	7.83
Vicat Softening Point (°C)	117.5	120.2	117.6	115.6
M_W/M_n	2.68	2.98	4.95	3.63
Extruder Amps	89	89	82	77
Extruder Die Pressure, psi (MPa)	5750 (40)	5770 (40)	5490 (38)	4390 (30)
Avg Haze Value, percent	14.2	11.5	11.6	9.6
DART (Method A), grams	272	264	272	234
DART (Method B), grams	186	152	172	112
Avg Elmendorf Type A CD, g	675	451	610	459
Avg Elmendorf Type A MD, g	294	210	232	254
Type A MD/CD	**0.44**	**0.46**	**0.38**	**0.55**
Avg Elmendorf Type B CD, g	862	850	738	542
Avg Elmendorf Type B MD, g	336	306	302	270
Type B MD/CD	**0.39**	**0.36**	**0.41**	**0.50**
CD-Avg Ultimate Tensiles, psi (MPa)	6352 (44)	6173 (43)	5573 (38)	5381 (37)
MD-Avg Ultimate Tensiles, psi (MPa)	6545 (45)	6196 (43)	6074 (42)	5872 (40)
Ultimate Tensiles MD/CD	**1.03**	**1.00**	**1.09**	**1.09**
HSIT, °C	~115	~115	~115	~110
HTIT, °C	~115	~114	~117	~110

Note: 2 mil blown film.
HSIT denotes heat seal initiation temperature.
HTIT denotes hot tack initiation temperature.
†Comparative example provided for purposes of comparison only; not an example of the present invention.

The data in Table 13 indicates that, surprisingly, Inventive Examples 22 and 23 provided significantly improved toughness properties, especially relative to comparative example 25, and comparable processability (that is, they have amperages and die pressures similar to the comparative examples) although their molecular weight distributions were substantially narrower than the comparative examples.

This Sheet Has Been Replaced
SEEN
REPLACED

* C L M S *

We claim:

1. A polymer composition comprising ethylene interpolymerized with at least one unsaturated comonomer, wherein the composition is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_2 in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities of greater than or equal to 0.926 g/cm^3 and is greater than 13°C at composition densities less than or equal to 0.92 g/cm^3.

2. A process for making an ethylene polymer composition comprised of ethylene interpolymerized with at

This Sheet Has Been Replaced

least one unsaturated comonomer and characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_2 in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities of greater than or equal to 0.926 g/cm^3 and is greater than 13°C at composition densities less than or equal to 0.92 g/cm^3,

the process comprising continuously operating at least two polymerization reactors.

This Sheet Has Been Replaced

SUBSTITUTE SHEET (RULE 26)

3. A fabricated article comprising an ethylene interpolymer composition which comprises ethylene interpolymerized with at least one unsaturated comonomer and is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_2 in the range of from greater than 6.6 to 8.2, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is less than or equal to 1, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, decreases with increased composition density such that ΔT is less than 23°C at composition densities of greater than or equal to 0.926 g/cm^3 and is greater than 13°C at composition densities less than or equal to 0.92 g/cm^3.

This Sheet Has Been Replaced
REPLACED

4. A polymer composition comprising ethylene interpolymerized with at least one unsaturated comonomer, wherein the composition is characterized as having:

a) a M_w/M_n of less than or equal to 3.3, as determined by gel permeation chromatography (GPC),

b) an I_{10}/I_2 ratio greater than 6.6, as determined in accordance ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg,

c) a composition density less than 0.945 gram/cubic centimeter, as determined according to ASTM-792,

d) at least two polymer components, the first component having a first viscosity average molecular weight, M_{v1}, and the second component having a second viscosity average molecular, M_{v2}, wherein M_{v1}/M_{v2} is in the range of from 0.6 to 1.2, as determined using ATREF-DV, and

e) a first ATREF peak temperature, T_{peak1} and a second ATREF peak temperature, T_{peak2}, corresponding to the at least two components and as determined using analytical temperature rising elution fraction (ATREF), wherein the temperature differential between T_{peak2} and T_{peak1}, ΔT, a ΔT which is equal to or less than the product of the equation:

$$\Delta T = [5650.842 \times \rho^2] - [11334.5 \times \rho] + 5667.93$$

wherein ΔT is in degrees Celsius and ρ is composition density in g/cm^3

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

SUBSTITUTE SHEET (RULE 26)

* C L M S *

5. The fabricated article of Claim 3 wherein the article is a film, film layer, coating, sealant, molding, pouch, bag, patch or sheet.

6. The fabricated article of Claim 5 wherein the film is a laminating film.

7. The fabricated article of Claim 5 wherein the film is in the form of a liner, trash-bag or heavy duty shipping sack.

8. The fabricated article of Claim 5 wherein the film is blown film.

9. The composition of Claim 1 wherein the at least one unsaturated comonomer is α-olefin selected from the group consisting of propylene, 1-butene, 1-isobutylene, 1-hexene, 4-methyl-1-pentene, 1-pentene, 1-heptene and 1-octene.

10. The process of Claim 2 wherein one of the at least two reactors is a recirculating loop reactor.

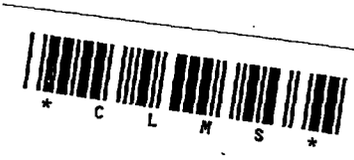
11. The process of Claim 2 wherein the at least two reactors are recirculating loop reactors.

12. The process of Claim 2 wherein the process comprises continuous solution polymerization.

13. The process of Claim 11 further comprising the steps of:

(i) feeding to the first reactor a constrained geometry catalyst system,

This Sheet Has Been Replaced



(ii) feeding to the second reactor a magnesium-supported titanium catalyst system characterized by a Mg:Ti molar ratio of 40 moles magnesium to less than 2 moles titanium and having a support surface area in the range of 400 to 430 m^2/g, and

(iii) operating the polymerization reaction system at a production split to the first reactor in the range of from 60 to 75 weight percent (based on the total incoming feed to the entire polymerization system),

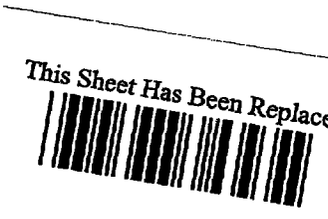
wherein each reactor is characterized as comprising at least one heat exchange apparatus.

14. The process of Claim 13 wherein the at least one heat exchange apparatus removes heat of reaction or polymerization from the reaction stream of the process at a rate of at least 7.4 $kW/m^3 \bullet °K$.

15. The composition of Claim 1 wherein the I_{10}/I_2 ratio is greater than or equal to 7.1, as determined in accordance with ASTM D-1238, Condition 190°C/2.16 kg and Condition 190°C/10 kg.

16. The composition of Claim 1 further characterized as having a density differential less than or equal to 0.028 g/cm^3, as measured in accordance with ASTM D-792.

17. The composition of Claim 1 wherein M_{v1}/M_{v2} is in the range of from 0.8 to 1, as determined using an ATREF-DV technique.



BEEN

* C L M S *

18. The composition of Claim 1 further characterized as having greater than or equal to 0.08 long chain branches per 10,000 carbons.

19. The composition of Claim 1 wherein at least one of the first polymer component or second polymer component is prepared using a homogeneous catalyst system.

20. The composition of Claim 19 wherein the homogenous catalyst system is a constrained geometry catalyst system.

21. The composition of Claim 1 wherein the first polymer component is prepared using a homogeneous catalyst system .

22. The composition of Claim 21 wherein the homogeneous catalyst system is a constrained geometry catalyst system and the second polymer component is prepared using a heterogeneous titanium, vanadium or zirconium catalyst system.

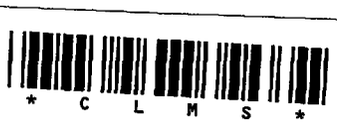
23. The composition of Claim 1 wherein the first polymer component is a substantially linear ethylene polymer.

24. The composition of Claim 23 wherein the second polymer component is a heterogeneously branched ethylene polymer.

25. The composition of Claim 1 wherein the first polymer component is a homogeneously branched linear ethylene polymer.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED



26. The composition of Claim 25 wherein the second polymer component is a heterogeneously branched ethylene polymer.

27. The composition of Claim 1 wherein both the first and second polymer components are homogeneously branched ethylene polymers.

28. The composition of Claim 27 wherein at least one of the homogeneously branched ethylene polymers is a substantially linear ethylene polymer.

29. The composition of any one of Claims 20, 23 or 28 wherein the substantially linear ethylene polymer is characterized as having:

(a) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63,$$

(b) a melt flow ratio, $I_{10}/I_2 \geq 5.63$, and

(c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer comprise the same comonomer or comonomers, the linear ethylene polymer has an I_2 and M_w/M_n within ten percent of the substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the

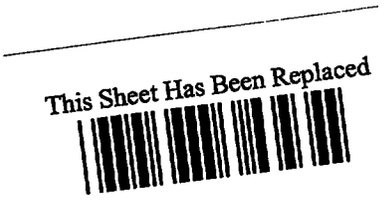
This Sheet Has Been Replaced



same melt temperature using a gas extrusion rheometer.

30. The composition of Claim 29 wherein the substantially linear ethylene polymer is further characterized as having a single DSC melting point and is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.





THIS SHEET HAS BEEN REPLACED