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(54) Title: EASIER PROCESSING POLYETHYLENE COMPOSITIONS WITH IMPROVED PHYSICAL PROPERTIES (57) Abstract Linear polyolefins, especially ethylene polymers are disclosed that exhibit improved processability over previously known linear polyethylenes. Inclusion of a high molecular weight component with a M_w greater than 120,000 into a lower molecular weight component with a M_w less than 120,000 provide improved processability. The high molecular weight component will have long chain branching. The improved processability will be reflected in a more shear sensitive polymer or polymer blend leading to lower power and torque to extrude these polymers. Additionally, the physical properties, such as dart drop impact are not negatively effected by the inclusion of the higher molecular weight component, and may be improved.		

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**TITLE: EASIER PROCESSING POLYETHYLENE COMPOSITIONS
WITH IMPROVED PHYSICAL PROPERTIES**

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FIELD OF THE INVENTION

This invention relates to metallocene catalyzed ethylene polymers which are more easily processed and exhibit superior toughness when compared to more conventional metallocene catalyzed ethylene polymers..

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BACKGROUND OF THE INVENTION

The production, fabrication, and use of linear polyolefin homopolymers and copolymers has increased steadily since their introduction in the 1940's. Advances in linear polyolefin technology have enabled the polymers to be used in a wide variety of end-use applications. Processes used to convert these polymers into useful items including film blowing, film casting, sheet extrusion, profile extrusion, injection molding, rotomolding, compression molding, thermoforming, a variety of fiber producing processes, and the like. In the 1970's new, more economical processes for the production of linear polyolefins came into wide use. During this period, the 1940's to the 1970's, the catalyst of choice by most polyolefin manufacturers in the world were generally of the traditional Ziegler-Natta (Z-N) type and the chromium types. Commercial use and exploitation of metallocene type catalyst systems began in the mid 1980s. These catalysts allow production of unique polymers compared to those produced with the more traditional catalysts. Many benefits accrue from metallocene catalyzed polyolefins which generally have relatively narrow molecular weight distribution (NMWD) and/or narrow composition distribution (NCD). Among these benefits are improved physical properties such as lower extractables, improved sealability, better clarity, and improved strength/toughness properties, especially impact resistance, puncture, and tensile strength as compared to the traditional Ziegler-Natta and chromium catalyzed products.

However these metallocene-catalyzed products share a disadvantage with traditional Ziegler-Natta polyolefins which also have relatively narrow MWDs, that disadvantage being poorer melt processability compared to, for instance, high pressure free radical initiated polyolefins. This disadvantage is seen in at least three

areas. First, these linear products are less shear thinning, that is their viscosity does not decrease as much with increasing shear rate compared to low density polyethylenes (LDPEs produced with free-radical processes) with which the linear materials often compete. The practical implication of this disadvantage is that
5 generally more power and torque are required to pump NMWD linear polymers through an extruder than is necessary for LDPE.

Second, in an extrusion die certain NMWD linear materials are prone to exhibit flow instabilities as they exit the die. These flow instabilities manifest themselves in poor appearance of the resulting film, often characterized as
10 sharkskinning or melt fracture. Sharkskinning is a defect which appears on the surface of extruded film or parts and consists of regularly spaced ridges generally perpendicular to the flow. Sharkskinning is generally dependent on flow rates and temperature. Melt fracture is a gross distortion in the extrudate which is thought to be more dependent on die geometry and generally occurs at higher shear rates than
15 sharkskinning.

A third processing deficiency of linear polyolefins is their relatively low melt strength which manifests itself in poor bubble stability in film blowing processes, weak parisons in blow molding processes, poor control over part thickness in thermoforming and the like when the linear polyolefins are processed
20 at relatively high temperatures and rates.

It is known in the industry that the processability of polyolefins can be improved by increasing their polydispersity index (PDI). For purposes of this application, the term PDI, and M_w/M_n (weight average molecular weight/number average molecular weight), will be used interchangeably. As PDI increases,
25 polyolefins generally exhibit more sheer thinning behavior, are less prone to flow instabilities, and frequently have higher melt strength. However, certain physical properties of these broader PDI polyolefins are generally defensive to narrower PDI linear polyolefins, especially those narrower linear polyolefins produced with metallocene catalysts. In particular, the Z-N and chromium catalyzed polymers
30 generally have higher extractables, lower strength / toughness properties, higher orientation, and poorer clarity and sealability than similar metallocene-catalyzed polymers.

One solution to the processability problems of the NMWD linear polyolefins has been to blend in more highly branched materials, usually LDPE,
35 which are more sheer sensitive and have good melt strength. The disadvantage of

this approach, as with many compromises, is that the excellent properties attributable to neat (non-blended) linear polyolefin polymers are rapidly diminished or compromised with the addition of relatively small amounts of these highly branched materials.

5 Other solutions to the processability problems of NMWD linear polyolefins have been attempted.

European Patent Application EP 0 124 722 A2 (US 4,586,995) describes a blend of two polymers, each having a weight average molecular weight between 120,000 and 160,000. The first polymer, which constitutes 40-95 weight percent of the blend, is an ethylene homopolymer or copolymer with a density >0.95 g/cc, an
10 energy of activation (E_a) <20 kcal/mole, and a long-chain branching (LCB) frequency <0.2 LCB / 1000 carbons. The second polymer, which constitutes 5-60 percent of the blend, contains 0.5-5 LCB / 1000 carbons, <10 short-chain branches, and has an $E_a >35$ kcal/mole. "Long-chain branches" are defined in EP
15 124 722 A2 as those side branches which are sufficiently long enough to affect the molecule's hydrodynamic volume. These branches are distinguishable from "short-chain branches" which are defined in the application as containing fewer than seven carbons and do not substantially effect hydrodynamic volume. Examples of short chain branches includes groups such as methyl, ethyl, propyl, butyl, amyl, and
20 hexyl.

The long chain branches in the second polymer disclosed in this document are produced by irradiation of a portion of the first polymer under non-gelling conditions in the absence of oxygen. This irradiation causes molecules with vinyl end groups or fragments from molecular scission to attach themselves to the
25 backbone of another polymer molecule, thus forming the "Y" structures referred to. These branched molecules are distinguishable from the branched molecules produced in high-pressure, free-radical polymerization processes (LDPE) by the relative level of short-chain branches in each. The Y-branched products contain fewer than one short-chain branches / 1000 carbons, the free radically polymerized
30 products contain 10-15 short chain branches / 1000 carbons.

In US Patent 5,272,236 substantially linear olefin polymers are disclosed which are said to have improved properties, specifically high melt elasticity, relatively narrow molecular weight distribution with good processability, and a substantial lack of melt fracture over a broad range of shear stress conditions.
35 Based on the example in the patent, these products appear to require about 18

percent less extrusion energy than their Ziegler-Natta analogs, and the dart impact resistance of the resulting film is within 5 percent of the Ziegler-Natta control. Also, noted in Tables VII and VIII of U.S. 5,272,236 many physical properties of films made from the polyolefins of the invention, are lower than those of the comparative example. Specific properties which show a decrease are tensile at yield, puncture propagation tear resistance (PPT) tear in the machine direction (MD), and puncture. Another property is substantially the same, elongation. Property improvements disclosed; MD tensile at break (7%), dart A (4%).

There has been a long-standing need in the polyolefins fabrication industry for the ever increasing strength/toughness properties of articles manufactured from linear polyolefins, combined with processability equivalent to or better than that of long-chain branched (free radical initiated) product such as LDPE.

SUMMARY

Certain embodiments of the present invention are directed to a polymer or polymer blend that satisfy the need for lower extrusion energy, while maintaining or improving most end use article mechanical properties.

In an embodiment of the present invention a linear polymer, typically a polyolefin, is given improved processability, substantial freedom from melt fracture and improved physical/mechanical properties, by the inclusion of long-chain branching. The long chain branching is found generally only on the higher molecular weight molecules in the product distribution. The high molecular weight entity of the product distribution will generally have a weight average molecular weight (M_w) typically greater than 120,000. The low molecular weight entity of the product distribution will generally have an M_w less than 120,000. This combination of lower molecular weight linear materials and higher molecular weight materials that contain long-chain branching can be achieved either through blending or through in-situ polymerization, which may involve a prepolymerization step. Ideally, the long-chain branches will be linear.

In an embodiment of the present invention a composition comprises an ethylene polymer having an extrusion torque less than 52 meters-gram (m-g) and a dart drop impact of at least 850 grams/mil. In another embodiment, a film is made from the composition.

These and other aspects, and advantages of certain embodiments of the present invention will become understood with reference to the following description and appended claims.

5 **DESCRIPTION**

Introduction

10 This invention concerns certain classes of polyethylene resins, their production and articles fabricated from these resins. These resins have unique properties which make them particularly well suited for use in producing certain classes of fabricated polymeric articles. Films and blow molded articles, for instance, have combinations of properties rendering them superior to articles and films previously available for many polymeric fabricated article applications. Additionally, the resins show a surprising increase in their ability to be melt processed. Following is a detailed description of certain preferred resins within the scope of this invention, preferred methods of producing these resins, and preferred applications of these resins. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention. For example, while the properties of resins are exemplified in film applications, they have numerous other uses. To the extent that this description is specific, this is solely for the purpose of illustrating preferred embodiments of this invention and should not be taken as limiting this invention to these specific embodiments.

25 It has been discovered that certain metallocene catalyst systems can be used in polymerization processes to produce resins having properties which are highly desirable for many classes of film extrusion, molding and certain other applications. Generally these resins have linear long-chain branches on typically the highest molecular weight molecules of a given population. When comonomer is present, it is generally more uniformly distributed than in Ziegler-Natta catalyzed or chromium catalyzed products. In these regards, the resin or resins of the present invention differ markedly from conventional Ziegler-Natta and from chromium catalyzed resins which are substantially free from long-chain branching and have non-uniform distribution of comonomer. They also differ from other attempts to introduce linear long-chain branching into linear molecules, in that the distribution of the long-chain branching of an embodiment of the present invention is limited substantially to the higher molecular weight population of materials. The ability to

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produce materials with linear long-chain branches on the highest molecular weight molecules of homopolymers or copolymers with relatively narrow composition distributions, has been heretofore unobtainable.

The metallocene catalyzed materials of certain embodiments of the present invention will have generally at least two components or groups of components a higher molecular weight group of components and a lower molecular weight group of components. Such combinations can be achieved by several schemes, including blending of independently produced or polymerized materials, polymerization in sequential reactors, prepolymerization of preferably the higher molecular portion or other schemes which will be known to those of ordinary skill in the art.

Lower Molecular Weight Component

The lower molecular weight component will generally have a MI greater than 1 dg/min; a molecular weight (M_w) below 120,000, the preferred range is 30,000 to 120,000, preferably in the range of from 50,000 to 120,000, more preferably in the range of from 70,000 to 120,000; a density in the range of from 0.90 g/cm³ to 0.97 g/cm³, preferably in the range of from 0.910 to 0.950, more preferably in the range of from 0.915 to 0.94, most preferably in the range of from 0.915 to 0.930 g/cm³; an M_w/M_n less than 6, preferably less than 5, more preferably than 4, most preferably less than 3; an energy of activation (E_a) less than 10 kcal/mole, preferably in the range of from 6 to 10, more preferably in the range of from 6.5 to 9, most preferably in the range of from 6.5 to 8.5 kcal/mole; and a CDBI greater than 50 percent.

The lower molecular weight component will generally be present in the combination in the range of from 50 to 99 weight percent, preferably in the range of from 70 to 99 weight percent, more preferably in the range of from 85 to 99 weight percent, most preferably in the range of from 90 to 99 weight percent based on the total weight of the combination.

Higher Molecular Weight Component

The higher molecular weight component will have: a MI less than 1 dg/min, preferably less than 0.5 dg/min; a molecular weight (M_w) greater than 120,000, preferably in the range of from 120,000 to 1,000,000, more preferably in the range of from 120,000 to 500,000, most preferably in the range of from 120,000 to 250,000; a density in the range of from 0.90 g/cm³ to 0.970 g/cm³,

preferably in the range of from 0.90 to 0.960, more preferably in the range of from 0.900 to 0.950, most preferably in the range of from 0.900 to 0.940 g/cm³; an M_w/M_n less than 6, preferably less than 5, more preferably less than 4, most preferably less than 3; a CDBI greater than 50 percent; an E_a greater than 12
5 kcal/mole, preferably in the range of from 12 to 30, more preferably in the range of from 12 to 25, most preferably in the range of from 12 to 20 kcal per mole.

The higher molecular weight component will be present in the combination in the range of from 1 to 50 weight percent, preferably in the range of from 1 to 30 weight percent, more preferably in the range of from 1 to 15 weight percent,
10 most preferably in the range of from 1 to 10 weight percent based on the total weight of the combination.

Both higher and lower molecular weight components will be ethylene homopolymers, ethylene- α -olefin copolymers, or combinations of homopolymers and copolymers. If one or both components are ethylene- α -olefin copolymers,
15 terpolymers and the like, the α -olefin or α -olefins may be the same or different in the high and low molecular weight components and the level of α -olefin or α -olefins incorporation may be the same or different. In either case, the α -olefin or α -olefins may be selected from those having 3 to 20 carbon atoms, preferably 4 to 10 carbon atoms, more preferably 6 to 8 carbon atoms. Most preferred α -olefins
20 are 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene and mixtures thereof. Preferably, when present, the α -olefin will be present in the ethylene- α -olefin copolymer or copolymers in the range of from 0.2 to 10 mole percent based on the total moles of monomer and comonomer incorporated into the copolymer, preferably in the range of 0.2 to 7.5 mole percent, more preferably in the range of
25 from 0.2 to 6.5 mole percent, most preferably in the range of from 0.2 to 5.5 mole percent.

Melt Processing

Melt processing of polymers represented by certain embodiments of the
30 present invention, will generally be characterized by reduced torque or power in a given piece of extrusion equipment, at a constant output (unit of weight/unit of time) compared to other metallocene catalyzed polyolefins, and Z-N catalyzed polyolefins. While the effects will be seen in larger equipment, routine laboratory testing can exhibit the effects, for instance, in a Haake Torque Rheometer. In such
35 a piece of equipment the torque at the conditions discussed below, the

compositions will exhibit torque less than 52 m-g preferably less than 50 m-g, more preferably less than 48 m-g, most preferably less than 46 m-g.

Fabricated Articles

5 Films, molded articles and the like made from these components may also include, in addition to the two aforementioned polyolefin components, other adjuvants and blend components that will be understood by those of ordinary skill in the art to be components and/or additives that may aid melt processing, prevent
10 oxidative damage, improve specific end use properties, and the like, all without substantial negative effect on either melt processability or physical properties of the fabricated article.

Such films may be used as stretch films (single or multi-layer), general packaging films, bags made from such films, and the like.

15 Other fabricated articles include extrusion blow-molded articles, injection molded articles, thermoformed articles and the like.

Films made from certain embodiments of the present invention will exhibit excellent dart drop impact. The dart drop impact will be at least 850 g/mil, preferably at least 950 g/mil, preferably at least 1,100 g/mil, more preferably at least 1,200 g/mil, most preferably at least 1,300 g/mil.

20

Test Methods

The resin and product properties cited in this specification were determined in accordance with the following test methods:

25

Table 1: Test Methods

Property	Units	Procedure
Melt Indices, Melt Flow Ratios	dg/min	ASTM D-1238
Density	g/cc	ASTM D-1505
Dart Drop Impact	g/mil	ASTM D-1709
Molecular Weight	-	Exxon Method
Energy of Activation (1)	kcal/mole	Exxon Method
Composition Distribution	-	Exxon Method
Extrusion Energy	amps or m-g	Exxon Methods

(1) Qualitative test for presence of long chain branching

Long-Chain Branching Position

One technique predicted to verify that the long chain branches are present only on the larger molecules of the invention is to first fractionate the material according to the procedure described by J. J. Watkins, et. al., in The Journal of
5 Supercritical Fluids, 1991, 4, 24-31, and then determine the Flow Activation Energy on each fraction. The fractions containing very low or no long chain branching should have the same E_a as linear molecules with the same short-chain branching frequency. The fractions containing long-chain branching should have a much higher E_a , after correcting the data for short-chain branching frequency.

10

Molecular Weight

The molecular weight distribution of a polymer can be determined with a Waters Gel Permeation Chromatograph equipped with Ultrastrogel columns and a refractive index detector. In this development, the operating temperature of the
15 instrument was set at 145°C, and the eluting solvent was trichlorobenzene. The calibration standards included sixteen polystyrenes of precisely known molecular weight, ranging from a molecular weight of 500 to a molecular weight of 5.2 million, and a polyethylene standard, NBS 1475.

The refractive index detector (DRI) detects polymeric molecules in the
20 GPC effluent which have been separated based on hydrodynamic volume. The assumption is that those molecules eluting through the detector at time T_x have the same molecular weight as those molecules in the linear calibration standard that elute at time T_x . However, it has been discovered that long chain branches do not increase the hydrodynamic volume of linear molecules by an amount proportional
25 to the length of these branches. It is believed that their contribution is only a fraction of the branch length. Therefore, if a long chain branched sample is analyzed with a refractive index detector calibrated with linear standards, the reported GPC moments will be low.

A low angle laser light scattering detector (LALLS), on the other hand,
30 produces a signal which is proportional to molecular weight, rather than hydrodynamic volume. Therefore, if the long chain branched sample is analyzed with both detectors, and M_w (DRI) < M_w (LALLS) then the difference between the two M_w 's is attributed to, and provides addition evidence of long chain branching. The difference in the M_w 's should indicate a minimum estimate of the
35 average branch length.

Energy of Activation

Evidence of long chain branching is provided by the magnitude of the product's E_a , energy of activation for viscous flow. The E_a of linear ethylene homopolymers is approximately 6.5 kcal/mole. The E_a of LDPEs is typically in the range of 11-15 kcal/mole. E_a is independent of molecular weight and polydispersity index, but does increase with increasing comonomer content and with increasing short chain branching length. Ethylene-hexene copolymers with densities greater than 0.900 contain less than 20 weight percent hexene-derived polymer units. The E_a of ethylene-hexene copolymers which contain less than 20 weight percent hexene-derived units is less than 8 kcal/mole. Therefore, an E_a greater than 8 kcal/mole is considered indicative of long chain branching in ethylene-hexene copolymers with densities greater than 0.900 g/cc.

E_a can be determined from parallel plate oscillatory shear melt viscoelastic measurements at four different temperatures. Zero shear viscosity at each temperature is plotted vs. the reciprocal of temperature. The slope of the linear regression of this plot is equal to E_a / R , where R is the gas constant, 1.987 cal/deg-mole.

Composition Distribution

Composition distribution is a measure of how uniformly a comonomer is distributed in a linear ethylene-based copolymer. Comonomer uniformity can be determined with a Temperature Rising Elution Fractionation (TREF) procedure similar to the one described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982). The test result is a distribution curve which illustrates the soluble fraction (weight percent) vs. temperature. The temperature scale is transformed to comonomer content using TREF data obtained with calibration standards which have very narrowly distributed, known comonomer levels.

The particular compositional attribute used in this development to distinguish between polymers is the breadth of the comonomer distribution, as indicated by its Composition Distribution Breadth Index (CDBI). CDBI is defined as the weight percent of the polymer molecules having a comonomer content within ± 50 percent of the median total molar comonomer content.

Extrusion Energy

Extrusion energy, i.e., the energy required to extrude a polyethylene product at a standard set of conditions, is expressed either as amps or torque.

- 5 In this development, torque was determined with a Rheomex Laboratory Single Screw Extrusion System, manufactured by Haake Buchler Instruments, Inc., Saddle Brook, NJ. The extrusion system was equipped with a 30 mil gap 4" sheet die, and a blunt tip, single flighted screw with the following description:

Screw type:	Single flighted, blunt tip
Number of working flights:	25 (15 feed/5 compression/5 metering)
Screw diameter:	3/4"
Screw length:	24.30"
Channel depth ratio:	3
Screw channel depth at feed opening:	0.15"
Screw flight width:	0.125"

- 10 Torque requirements were determined for comparative examples 7, 9, and 12-19 at 190°C and 128 rpm Table 2. Results are summarized in following table, and are illustrated in Figure 1.

Table 2: Extrusion Torque of LDPEs and LLDPEs

15

Comparative Example	Catalyst/Initiator	MI	Torque (1)
7	Ziegler-Natta	0.97	53
9	Metallocene	3.00	56
12	Ziegler-Natta	1.06	54
13	Ziegler-Natta	1.92	52
14	Ziegler-Natta	2.16	50
15	Ziegler-Natta	3.06	42
16	Perester	0.32	42
17	Perester	1.00	32
18	Perester	2.00	29
19	Perester	2.00	29

(1) @ 128 rpm and 190°C

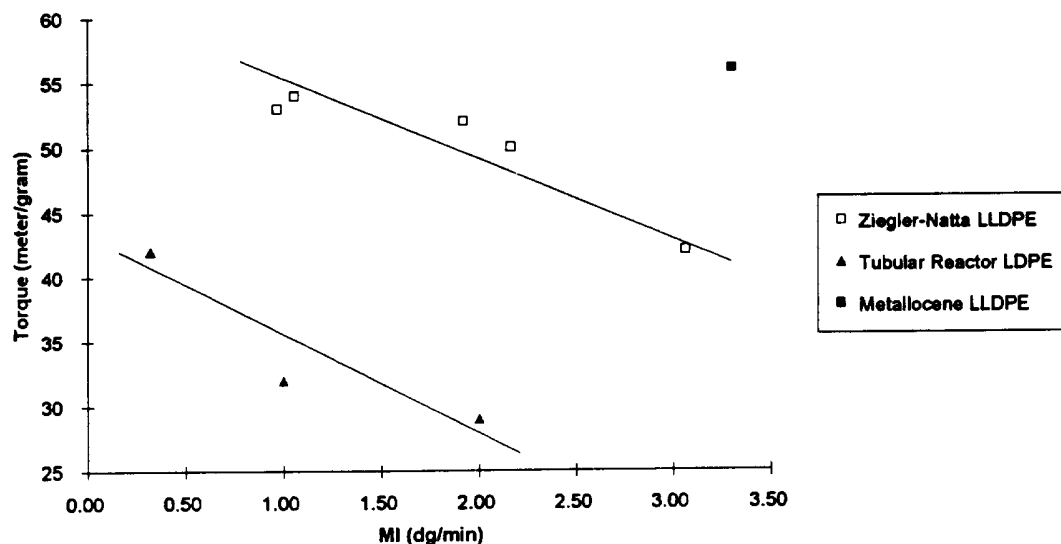


Figure 1: Extrusion torque at 128 rpm and 190°C for LDPE and two types of LLDPE

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Amps was determined with both 2 1/2" and 3 1/2" film line extruders. Results at extrusion rates between 8 and 12 lb/hr/inch of die circumference through die gaps between 30 and 90 mils at temperatures between 375 and 450°F with experimental products were compared to the same LDPE and Ziegler-Natta LLDPE controls cited above at equivalent conditions.

10

Examples

All materials, unless otherwise noted, may be obtained from Exxon Chemical Company.

15

Comparative Example 1

Comparative Example 1 is a linear ethylene-hexene copolymer produced in a gas phase process with a silica-supported, bis(1-methyl-3-n-butyl-cyclopentadienyl) zirconium dichloride / methyl alumoxane catalyst (not available commercially). M_w , MI, density, and melt flow ratio are 131,000, 0.6, 0.921, and 15.9, respectively.

20

Comparative Example 2

Comparative Example 2 is a blend composed of 7 weight percent Escorene LD-113 and 93 weight percent Comparative Example 1. Escorene LD-113 is a commercially available long-chain branched ethylene homopolymer produced in a high-pressure, tubular reactor with a peroxide initiator. Target MI and density of LD-113 are 2.3 and 0.921, respectively.

Comparative Example 3

Comparative Example 3 is a linear ethylene-hexene copolymer produced in a gas phase process with a silica-supported, bis(1-methyl-3-n-butyl-cyclopentadienyl) zirconium dichloride / methyl alumoxane catalyst (not available commercially). M_w , MI and density are 119,000, 0.83 and 0.920, respectively.

Comparative Example 4

Comparative Example 4 is a blend composed of 3 weight percent Escorene HD-7000F and 97 weight percent Comparative Example 3. Escorene HD-7000F is a commercially available linear ethylene-butene copolymer produced in a series slurry process with a titanium-based Ziegler-Natta catalyst. Target MI and density of the HD-7000F are 0.045 and 0.952, respectively. Typical M_w of HD 7000F is > 200,000.

Comparative Example 5

Comparative Example 5 is a blend composed of 3 weight percent Escorene HD-9856B and 97 weight percent Comparative Example 3. Escorene HD-9856B is a commercially available linear ethylene-butene copolymer produced in a series slurry process with a titanium-based Ziegler-Natta catalyst. Target MI and density of the HD-9856B are 0.46 and 0.956, respectively. Typical M_w of HD 9856 B is 140,000.

Comparative Example 6

Comparative Example 6 is a blend composed of 6 weight percent Escorene HD-9856B and 94 weight percent Comparative Example 3. Escorene HD-9856B is described in Comparative Example 5.

Comparative Example 7

Comparative Example 7 is Escorene LL-3001.63, a commercially available linear ethylene-hexene copolymer produced in a gas phase reactor with a titanium-based Ziegler-Natta catalyst. Typical M_w , MI, density, and melt flow ratio are
5 110,000, 1.9, 0.922, and 27, respectively.

Comparative Example 8

Comparative Example 8 is a blend composed of 30 weight percent LD-113 and 70 weight percent of the resin described in Comparative Example 7. LD-113 is
10 described in Comparative Example 2.

Comparative Example 9

Comparative Example 9 is a linear ethylene-hexene copolymer produced in a gas phase process with a silica-supported, bis(1-methyl-3-n-butyl-cyclopentadienyl) zirconium dichloride / methyl alumoxane catalyst (not available
15 commercially). M_w , MI, density, and melt flow ratio are 80,000, 3.04, 0.919, and 17.316.8, respectively.

Comparative Example 10

Comparative Example 10 is a linear ethylene-hexene copolymer produced in a gas phase process with a silica-supported, bis(1-methyl-3-n-butyl-cyclopentadienyl) zirconium dichloride/methyl alumoxane catalyst (not available
20 commercially). M_w , MI, density, and melt flow ratio are 80,000, 3.31, 0.919, and 17.3, respectively.

25

Examples 1, 3, 9, and 10 are prepared according to a process disclosed in WO 94/26816 incorporated herein by reference for purposes of U. S. Patent practice.

Example 11

Example 11 is a blend composed of 95 weight percent Comparative Example 10 and 5 weight percent B1 which is a high molecular weight, linear ethylene-hexene copolymer and which contains linear long chain branching. B1 was prepared by adding 180 psig ethylene, 8 ml hexene-1, and a mono-Cp catalyst
35 (dimethyl(tetramethylcyclopentadienyl)cyclododecylamidosilyl titanium dichloride)

with a methyl-alumoxane activator to 500 ml toluene in a 2-liter autoclave reactor. The reactor temperature was relatively controlled at 90°C, and the polymerization was terminated after 15 minutes. The resulting product had a density of 0.912 g/cc, an E_a of 14.1 kcal/mole, an M_w of 206,000 (DRI detector) and 231,000 (LALLS detector), a polydispersity of 2.56 (DRI detector, uncorrected for long chain branching); and a average butyl branching content of 22 br/1000 carbons.

Comparative Example 12

Comparative Example 12 is Escorene LL-1001.30, a commercially available linear ethylene-butene copolymer produced in a gas phase reactor with a titanium-based Ziegler-Natta catalyst. MI is 1.06 dg/min., typical density is 0.918 g/cc.

Comparative Example 13

Comparative Example 13 is Escorene LL-3002.37, a commercially available linear ethylene-hexene copolymer produced in a gas phase reactor with a titanium-based Ziegler-Natta catalyst. MI is 1.92 dg/min., typical density is 0.918 g/cc.

Comparative Example 14

Comparative Example 14 is Escorene LL-1002.09, a commercially available linear ethylene-butene copolymer produced in a gas phase reactor with a titanium-based Ziegler-Natta catalyst. MI is 2.16 dg/min., typical density is 0.918 g/cc.

Comparative Example 15

Comparative Example 15 is Escorene LL-3003.32, a commercially available linear ethylene-hexene copolymer produced in a gas phase reactor with a titanium-based Ziegler-Natta catalyst. MI is 3.06 dg/min., typical density is 0.918 g/cc.

Comparative Example 16

Comparative Example 16 is LD-141.87, a commercially available long-chain branched ethylene-vinyl acetate copolymer produced in a high-pressure,

tubular reactor with a peroxide initiator. Target MI, density, and VA content are 2.3 dg/min, 0.921 g/cc, and 2%, respectively.

Comparative Example 17

- 5 Comparative Example 17 is LD-312.09, a commercially available long-chain branched ethylene-vinyl acetate copolymer produced in a high-pressure, tubular reactor with a peroxide initiator. MI is 1.00 dg/min., typical density and VA content are 0.927 g/cc and 4.6 weight percent, respectively.

Comparative Example 18

10 Comparative Example 18 is LD-105.30, a commercially available long-chain branched polyethylene-homopolymer produced in a high-pressure, tubular reactor with a peroxide initiator. MI is 2.00 dg/min., typical density is 0.925 g/cc.

Comparative Example 19

15 Comparative Example 19 is LD-306.09, a commercially available long-chain branched ethylene-vinyl acetate copolymer produced in a high-pressure, tubular reactor with a peroxide initiator. MI is 2.00 dg/min., typical density and VA content are 0.926 g/cc and 5.5 weight percent, respectively.

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 Polyethylene products may be distinguished from each other by, for instance, their processability and their end-use properties. These attributes may be predicted by, among other things, the catalyst and process used to produce the product, (which define the product's molecular weight and comonomer distributions), and on the product's melt index, density, and comonomer type. Blending different products together allows converters to combine certain advantages of the individual blend components. One combination which has been quite popular since linear polyethylenes (Z-N and/or chromium catalyzed) were first introduced is LLDPE plus LDPE, with the LLDPE content generally ≥ 70 weight percent.

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 LLDPEs can be drawn down to relatively thin gauges, and have higher modulus and significantly better strength/toughness properties than LDPEs. However, LLDPEs have lower melt strength, require more extrusion energy, and are hazier than LDPEs. LDPEs, on the other hand, have higher melt strength and good clarity. The combination succeeds in improving LLDPE's melt strength and

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clarity, while retaining LLDPE's good drawability, but generally does not improve LLDPE's extrusion energy or mechanical properties. Certain blend ratios, e.g., 70-80 percent LLDPE / 20-30 percent LDPE, are antagonistic relative to dart impact and tear resistance, i.e., the dart and tear of the blend is generally poorer than either the blend components by themselves.

Table 3: LLDPE vs. LLDPE / LDPE Blends

Comparative Example	1	2	7	8
LDPE Content	-	7%	-	30%
Blending Procedure	-	Melt	-	Melt
Blown Film Extruder	3 1/2" Sano	3 1/2" Sano	2 1/2" Egan	2 1/2" Egan
Dart Impact (g/mil)	1420	530	180	40
Elmendorf MD Tear (g/mil)	430	115	360	20
Extrusion Amps (1)	173	170	44	39

(1) At constant output

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In Table 3, note the substantial decreases in both dart impact and tear resistance when LDPE is added to the linear copolymers. The reduction in extrusion energy with the addition of 7 percent LDPE is almost negligible; the reduction with the addition of 30 percent is, understandably, greater. Clearly, the toughness / processability balance has not been improved.

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It has been discovered that if the LDPE component in these blends is replaced with copolymer B1, the dart impart of film made with the blend does not decrease. Instead, it increases substantially, from 612 g/mil to >1430 g/mil. In addition, the Elmendorf MD Tear of the LLDPE/B1 blend decreases only slightly, compared to the substantial decrease in the LLDPE/LDPE blends included in Table 2. Finally, the torque required to extrude the blend at 128 rpm and 190°C was 20 percent lower than the torque required to extrude the principal component (Comparative example 10) by itself. Clearly, the addition of 5 percent B1 has resulted in a substantial improvement in the toughness / processability balance of this LLDPE.

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Table 4: LLDPE vs. LLDPE / B1 Blend

	Comparative Example 10	Example 11
B1 Content	-	5%
Blending Procedure	-	Melt
Cast Film Extruder	1" Killian	1" Killian
Dart Impact (g/mil)	612	>1430
Elmendorf MD Tear (g/mil)	188	160
Torque (m-g) @ 128 rpm, 190°C	56	45

B1 is a 0.912 g/cc density, linear ethylene-hexene copolymer with a relatively high molecular weight and an E_a of 14 kcal/mole. Details of its preparation appear in Example 11.

In order to verify that these enhancements were not due to the higher molecular weight of B1, a series of blends were evaluated in which B1 was replaced with a high molecular weight polyethylene (HMW-PE) which contains <3 short chain branches / 1000 carbons and no long chain branching. Results appear in Table 5.

Table 5: LLDPE vs. LLDPE / HMW-PE Blends

Comparative Example	3	4	5	6
HMW-PE Content (%)	-	3	3	6
Blending Procedure	-	Dry		Dry
Blown Film Extruder	(1)	(1)	(1)	(1)
Dart Impact (g/mil)	898	869 (2)	740	712
Elmendorf MD Tear (g/mil)	215	227	238	206
Extrusion Amps (3)	156	157		157

- (1) 3 1/2" Sano
 (2) 523 g/mil after melt compounding
 (3) At constant temperature (440-445°F) and output (325 lb/hr)

All appear to have equivalent extrusion energy requirements. The addition of these types of HMW-PEs has a slight adverse effect on dart impact. These

blends do not have improved toughness / processability balance shown by the B1 blends shown in Table 3.

5 The present invention is distinguishable from known polyethylenes on the basis of the nature and positioning of the long chain branches, and on the combination of reduced extrusion energy and substantially enhanced film impact resistance. The long chain branches are of sufficient length, frequency, and intramolecular position to produce a component with an E_a greater than 12 kcal/mole. They are more compatible with the linear blend component, and produces the appropriate solid state thermoplastic networks to deliver enhanced mechanical properties.

10 The ethylene copolymers described herein may be made from ethylene and an alpha-olefin where the alpha-olefin has in the range of from 4 to 20 carbon atoms, preferably in the range of from 4 to 10 carbon atoms, most preferably in the range of from 4 to 8 carbon atoms. The choice of comonomer for the lower molecular weight component and the higher molecular weight component can be based on having the same alpha-olefin as the comonomer or different alpha-olefins as comonomers (for instance, lower molecular weight material may have a butene comonomer, the higher molecular weight material may have an octene comonomer). The level of comonomer incorporation in the members of the combination may be same or may be different. In general the range of comonomer incorporation in copolymers described by an embodiment of the present invention are dependent on the type of comonomer.

20 Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, means of forming heterogeneous particles, and other combinations of polymers are contemplated. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

Claims:**I Claim:**

1. A composition comprising an ethylene polymer wherein said composition
5 includes:
a) a first component, said first component present in said composition in
the range of from 50 to 99 weight percent, based on the total weight of said
composition wherein said first component has;
i) an M_w less than 120,000;
10 ii) an E_a less than 10 kcal/mole;
iii) an M_w/M_n less than 6;
iv) a CDBI greater than 50 percent;
b) a second component, said second component present in said
composition in the range of from 50 to 1 weight percent based on the total weight
15 of said composition, wherein said second component has;
i) an M_w greater than 120,000;
ii) an E_a greater than 12 kcal/mole;
iii) an M_w/M_n less than 6;
iv) a CDBI greater than 50 percent
20 said composition having extrusion torque less than 52 m-g, preferably less than 50,
more preferably less than 48 m-g, and a dart drop impact of at least 850 g/mil,
preferably at least 950 g/mil, more preferably at least 1,100 g/mil.
2. The use of the composition of claim 1 as a film or a molded article.
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3. The composition of Claim 1 wherein said second component has an E_a in
the range of from 12 to 20 kcal/mole, an M_w/M_n less than 3 and an M_w in the
range of from 120,000 to 500,000.
- 30 4. A film comprising a polyethylene composition, said composition including:
a) in the range of from 90 to 99 weight percent of a first polyethylene;
b) in the range of from 1 to 10 weight percent of a second polyethylene,
all weight percents based on the total weight of said polyethylene composition;
wherein said first polyethylene has;
35 i) an M_w in the range of from 70,000 to 120,000;

- ii) a density in the range of from 0.915 g/cm³ to 0.930 g/cm³;
- iii) a M_w/M_n below 3 ;
- iv) an E_a in the range of from 6.5 to 8.5 kcal/mole;
- v) a CDBI greater than 50 percent;

5 wherein said second polyethylene has:

- i) a M_w in the range of from 120,000 to 250,000;
- ii) a density in the range of from 0.90 g/cm³ to 0.95 g/cm³;
- iii) a M_w/M_n below 3 ;
- iv) an E_a in the range of from 12 to 20 kcal/mole; and
- 10 v) a CDBI greater than 50 percent.

5. The film of Claim 4 wherein said first polyethylene is an ethylene α -olefin copolymer containing in the range of from 0.2 to 10 weight percent of said α -olefin, said mole percent based on the total moles of said ethylene α -olefin copolymer, said α -olefin being selected from the group consisting of 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene.

6. The film of Claim 5 wherein said second polyethylene is an ethylene- α -olefin copolymer containing in the range of from 0.2 to 10 mole percent of said α -olefin based on the total moles of said second polyethylene, said α -olefin selected from the group consisting of 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene, wherein said second polyethylene has a M_w in the range of from 120,000 to 250,000.

25 7. A polyethylene film comprising:

- a) a first ethylene α -olefin copolymer, said first ethylene- α -olefin copolymer being present in said film in the range of 90 to 99 weight percent based on the total weight of said polyethylene film, said first ethylene- α -olefin copolymer having an α -olefin content in the range of from 0.2 to 10 mole percent based on the total moles of said first ethylene- α -olefin copolymer, said α -olefin is selected from the group consisting of 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene, said first ethylene- α -olefin copolymer having:
 - i) an M_w in the range of from 70,000 to 120,000;
 - ii) a density in the range of from 0.915 to 0.930 g/cm³;
 - 35 iii) an E_a in the range of from 6.5 to 8.5 kcal/mole;

- iv) a CDBI greater than 50 percent; and
- b) a second ethylene- α -olefin copolymer, said first ethylene- α -olefin copolymer being present in said film in the range of 1 to 10 weight percent based on the total weight of said polyethylene film, said first ethylene- α -olefin copolymer having an α -olefin content in the range of from 0.2 to 10 mole percent based on the total moles of said first ethylene- α -olefin copolymer, said α -olefin is selected from the group consisting of 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene, said first ethylene- α -olefin copolymer having;
- 5 i) an M_w in the range of from 120,000 to 250,000;
- 10 ii) a density in the range of from 0.915 to 0.930 g/cm³;
- iii) an E_a in the range of from 12 to 20 kcal/mole;
- iv) a CDBI greater than 50 percent; and
- wherein said first and said second ethylene- α -olefin copolymers are extruded with an extrusion torque of less than 48 m-g and wherein said polyethylene film has a
- 15 dart drop impact of at least 1,100 g/mil.
8. Use of the film of claims 4 or 7 or the composition of claim 1 as a stretch wrap.
9. The film of claims 4 or 7, wherein said film has a dart impact above 1000 g/mil.
- 20 10. Use of the film of claims 4 or 7 as a bag.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16534

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 210 142 (KALE LAWRENCE T ET AL) 11 May 1993 see claims ---	1-10
A	EP,A,0 274 536 (MITSUI PETROCHEMICAL IND) 20 July 1988 see claims ---	1-10
A	ANGEWANDTE MAKROMOLEKULARE CHEMIE, vol. 200, 1 September 1992 pages 15-25, XP 000305374 ABRAHAM D ET AL 'STUDIES ON LDPE/LLDPE BLENDS' see page 17, table 1, specimens 2A and 3A --- -/--	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, vol. 18, no. 10, 1 January 1991 pages T67-T68, XP 000249219 MASHUKOV N I 'PROPERTIES OF BLENDS OF HIGH-DENSITY POLYETHYLENES WITH DIFFERENT MOLECULAR MASS CHARACTERISTICS' -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/16534

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		JP-A- 63012606	20-01-88
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		WO-A- 8800212	14-01-88
		US-A- 5019627	28-05-91