EXHIBIT A

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Chum et al.

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[54] **ETHYLENE POLYMER FILM MADE FROM ETHYLENE POLYMER BLENDS**

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[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **834,050**

[22] Filed: **Apr. 11, 1997**

Related U.S. Application Data

[63] Continuation of Ser. No. 544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/08**

[52] **U.S. Cl.** **525/240**

[58] **Field of Search** 525/240

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[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

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FIGURE 1

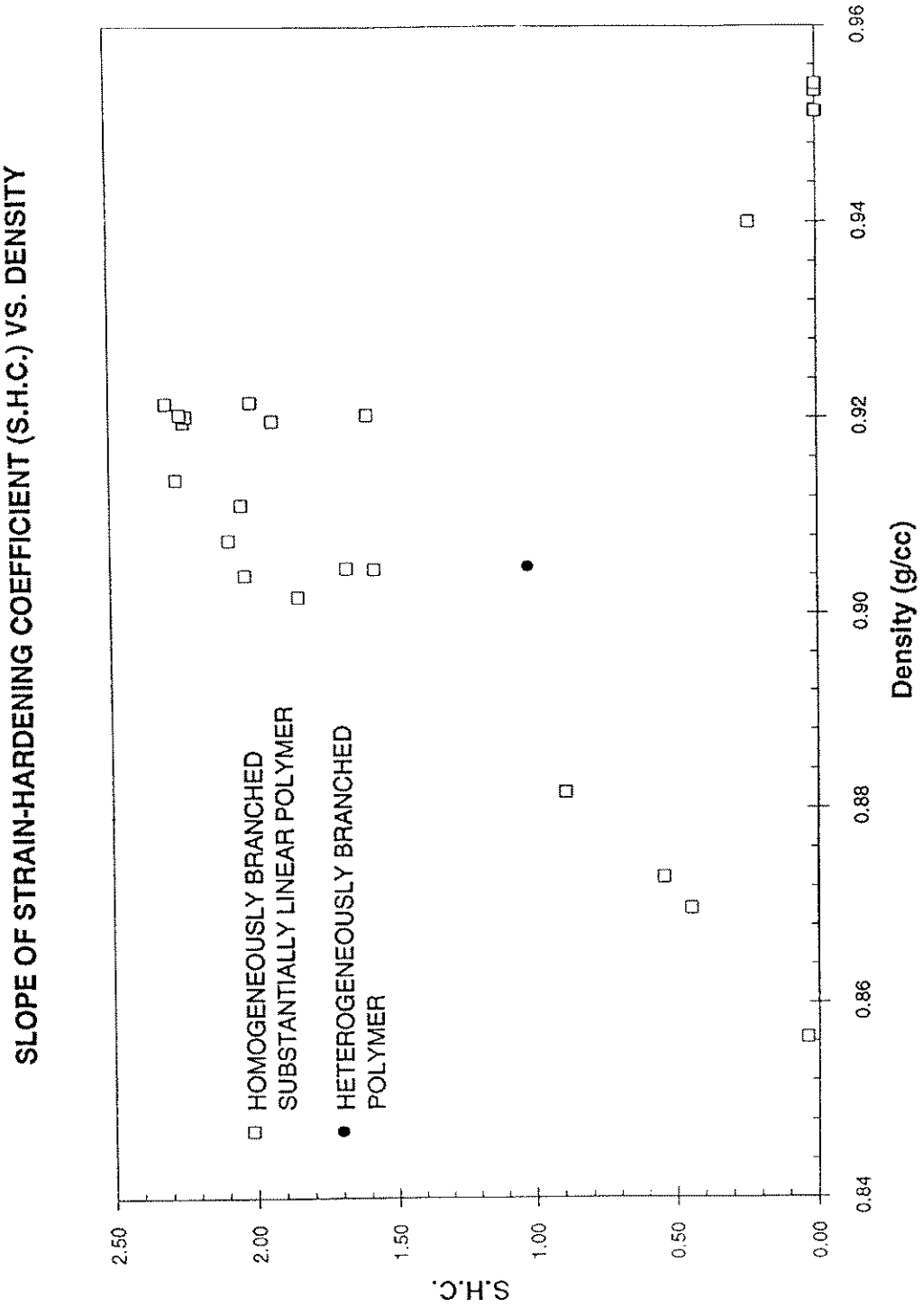
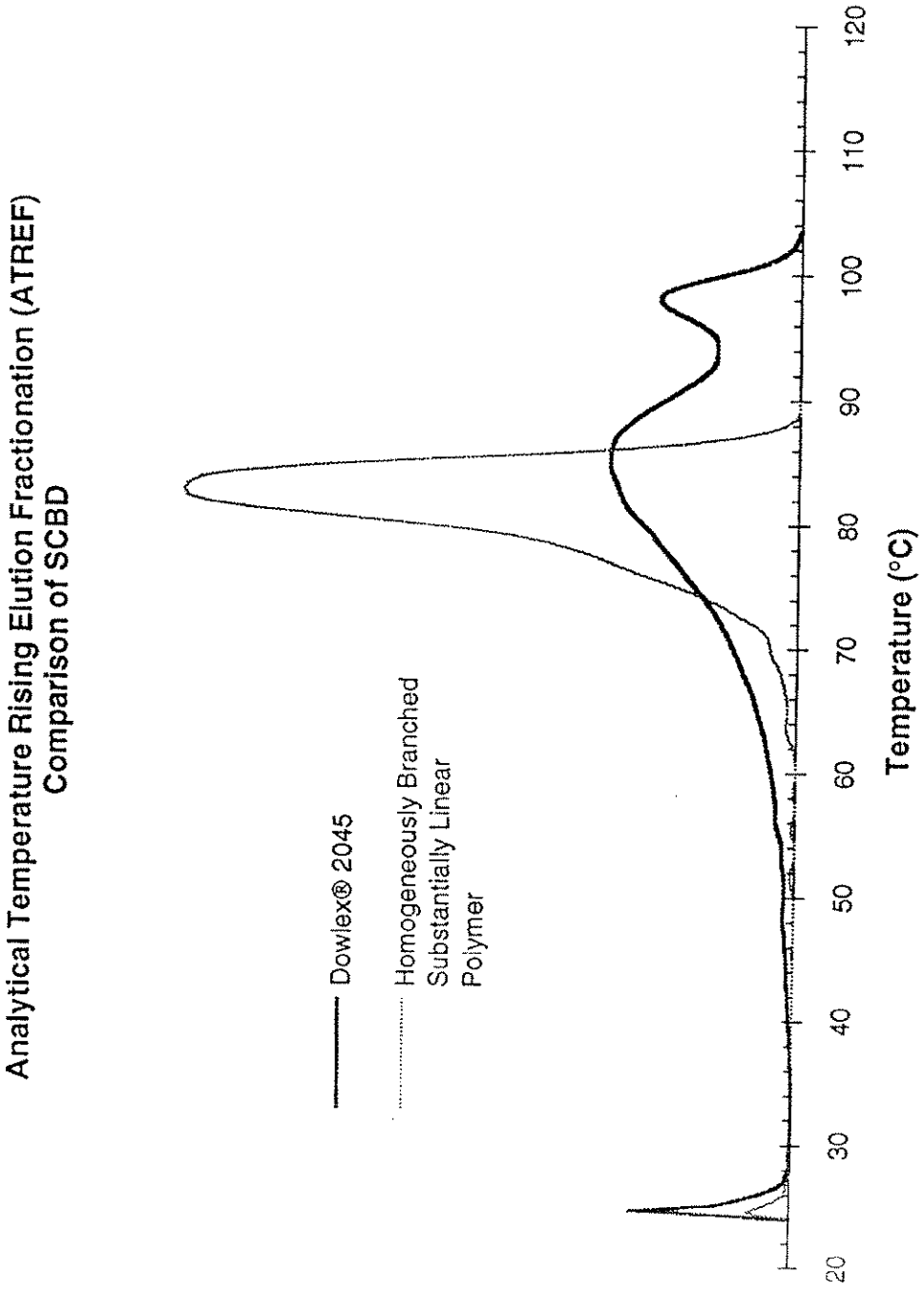

SLOPE OF STRAIN-HARDENING COEFFICIENT (S.H.C.) VS. DENSITY
S.H.C.
2.50
2.00
1.50
1.00
0.50
0.00
Density (g/cc)
0.84
0.86
0.88
0.90
0.92
0.94
0.96
HOMOGENEOUSLY BRANCHED SUBSTANTIALLY LINEAR POLYMER
HETEROGENEOUSLY BRANCHED POLYMER

Figure 2


Analytical Temperature Rising Elution Fractionation (ATREF)
Comparison of SCBD
Dowlex® 2045
Homogeneously Branched
Substantially Linear
Polymer
20
30
40
50
60
70
80
90
100
110
120
Temperature (°C)

ETHYLENE POLYMER FILM MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Rule 1.60 continuation application of application Ser. No. 08/544,497, filed Oct. 18, 1995, now issued U.S. Pat. No. 5,677,383, which was a Rule 1.60 continuation application of application Ser. No. 08/378,998, filed Jan. 27, 1995, now abandoned, which was a Rule 1.62 continuation application of application Ser. No. 08/054,379, filed Apr. 28, 1993, now abandoned, which was a continuation-in-part application of Ser. No. 07/776,130, filed Oct. 15, 1991, now issued U.S. Pat. No. 5,272,236, the disclosures of each of which are incorporated herein in their entirety by reference. This application is also related to application Ser. No. 08/475,737, filed Jun. 7, 1995, now abandoned; application Ser. No. 07/939,281, filed Sep. 2, 1992, now issued U.S. Pat. No. 5,278,272; and application Ser. No. 08/510,527, filed Aug. 2, 1995, now abandoned which is a continuation application of application Ser. No. 08/010,958, filed Jan. 29, 1993, now abandoned; the disclosures of each of which are incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to compositions comprising specific ethylene/α-olefin polymer blends.

The polymer blends preferably comprise:

(A) at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having specific processing characteristics, blended together with

(B) a heterogeneously branched ethylene polymer.

Such compositions are particularly useful in film applications (e.g., high strength thin gauge packaging film or heat sealable packaging film).

BACKGROUND OF THE INVENTION

Thin film products fabricated from linear low density polyethylene (LLDPE) and/or high density polyethylene (HDPE) are widely used for packaging applications such as merchandise bags, grocery sacks, and industrial liners. For these applications, films with high tensile strength, as well as high impact strength, are desired because film producers can down gauge their film products and still retain packaging performance.

Previous attempts were made to optimize film tensile strength and yield strength by blending various heterogeneous polymers together on theoretical basis. While such blends exhibited a synergistic response to increase the film yield strength, the film impact strength followed the rule of mixing, often resulting in a "destructive synergism" (i.e., the film impact strength was actually lower than film made from one of the two components used to make the blend).

For example, it is known that while improved modulus linear polyethylene resin can be produced by blending high density polyethylene with a very low density polyethylene (VLDPE), the impact strength of the resin blend follows the rule of mixing.

There is a continuing need to develop polymers which can be formed into fabricated articles (e.g., film) having these combinations of properties (e.g., improved modulus, yield strength, impact strength and tear strength). The need is especially great for polymers which can be made into film which can also be down gauged without loss of strength properties, resulting in savings for film manufacturers and consumers, as well as protecting the environment by source reduction.

Surprisingly, we have now discovered that film can have synergistically enhanced physical properties, when the film is made from a blend of at least one homogeneously branched ethylene/α-olefin interpolymer and a heterogeneously branched ethylene/α-olefin interpolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows the relationship between the density and the slope of strain hardening coefficient for homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions disclosed herein, in comparison with a heterogeneously branched ethylene/α-olefin copolymer.

FIG. **2** shows the short chain branching distribution (as measured by analytical temperature rising elution fractionation (ATREF)) for a homogeneously branched substantially linear ethylene/1-octene copolymer used in the invention, in comparison with Dowlex™ 2045 (a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company).

SUMMARY OF THE INVENTION

Formulated ethylene/α-olefin compositions have now been discovered to have improved physical and mechanical strength and are useful in making fabricated articles. Films made from these novel compositions exhibit surprisingly good impact and tensile properties, and an especially good combination of modulus, yield, ultimate tensile, and toughness (e.g., Dart impact).

The compositions comprise (A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of

at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

In another aspect, the compositions comprise from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of:

(A) at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

Preferably, both the homogeneously branched substantially linear ethylene/α-olefin interpolymer and the homo-

geneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.3.

DETAILED DESCRIPTION OF THE INVENTION

The homogeneously branched ethylene/α-olefin interpolymer is preferably a homogeneously branched substantially linear ethylene/α-olefin interpolymer as described in pending U.S. Ser. No. 07/776,130 now U.S. Pat. No. 5,272, 236. The homogeneously branched ethylene/α-olefin interpolymer can also be a linear ethylene/α-olefin interpolymer as described in U.S. Pat. No. 3,645,992 (Elston), the disclosure of which is incorporated herein by reference.

The substantially linear ethylene/α-olefin interpolymers are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene (e.g., Ziegler polymerized linear low density polyethylene (LLDPE)), nor are they highly branched polymers, as used to describe low density polyethylene (LDPE).

The substantially linear ethylene/α-olefin interpolymers of the present invention are herein defined as in copending application Ser. No. 07/776,130 now U.S. Pat. No. 5,272, 236 and in copending application entitled "Elastic Substantially Linear Olefin Polymers" filed Sep. 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens.

The homogeneously branched ethylene/α-olefin interpolymers useful for forming the compositions described herein are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The homogeneity of the interpolymers is typically described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), in U.S. Pat. No. 4,798,081 (Hazlitt et al.), or in U.S. Pat. No. 5,089,321 (Chum et al.) the disclosures of all of which are incorporated herein by reference. The SCBDI or CDBI for the linear and for the substantially linear olefin polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent. The homogeneous ethylene/α-olefin polymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons). The homogeneously branched ethylene/α-olefin polymers also do not contain any highly short chain branched fraction (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching equal to or more than about 30 methyls/ 1000 carbons).

The substantially linear ethylene/α-olefin interpolymers for use in the present invention typically are interpolymers of ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefins. Copolymers of ethylene and 1-octene are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Ethylene copolymerized with two or more comonomers can also be used to make the homogeneously branched substantially linear interpolymers useful in this invention. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The term "linear ethylene/α-olefin interpolymer" means that the interpolymer does not have long chain branching. That is, the linear ethylene/α-olefin interpolymer has an absence of long chain branching, as for example the linear low density polyethylene polymers or linear high density polyethylene polymers made using uniform (i.e., homogeneous) branching distribution polymerization processes (e.g., as described in U.S. Pat. No. 3,645,992 (Elston)) and are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The term "linear ethylene/α-olefin interpolymer" does not refer to high pressure branched (free-radical polymerized) polyethylene which is known to those skilled in the art to have numerous long chain branches. The branching distribution of the homogeneously branched linear ethylene/α-olefin interpolymers is the same or substantially the same as that described for the homogeneously branched substantially linear ethylene/α-olefin interpolymers, with the exception that the linear ethylene/α-olefin interpolymers do not have any long chain branching. The homogeneously branched linear ethylene/α-olefin interpolymers comprise ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefin. Copolymers of ethylene and 1-octene are especially preferred. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1 -pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Both the homogeneously branched substantially linear and linear ethylene/α-olefin interpolymers have a single melting point, as opposed to traditional heterogeneously branched Ziegler polymerized ethylene/α-olefin copolymers having two or more melting points, as determined using differential scanning calorimetry (DSC).

The density of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally from about 0.89 g/cm^3 to about 0.935 g/cm^3, preferably from about 0.905 g/cm^3 to about 0.925 g/cm^3, and especially from about 0.905 g/cm^3 to less than about 0.92 g/cm^3.

The amount of the homogeneously branched linear or substantially linear ethylene/α-olefin polymer incorporated into the composition varies depending upon the heterogeneously branched ethylene polymer to which it is combined. However, about 50 percent (by weight of the total composition) of the homogeneous linear or substantially linear ethylene/α-olefin polymer is especially preferred in the novel compositions disclosed herein.

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention 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 lower melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

Another measurement useful in characterizing the molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of the I_{10} and I_2 melt index terms is the melt flow ratio and is designated as I_{10}/I_2. Generally, the I_{10}/I_2 ratio for the homogeneously branched linear ethylene/α-olefin interpolymers is about 5.6. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 ratio, the more long chain branching in the interpolymer. Generally, the I_{10}/I_2 ratio of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is at least about 6, preferably at least about 7, especially at least about 8 or above. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers, the higher the I_{10}/I_2 ratio, the better the processability.

Other additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), phosphites (e.g., Irgafos® 168 also made by Ciba Geigy Corp.)), cling additives (e.g., PIB), antiblock additives, pigments, fillers, and the like can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants.

Molecular Weight Distribution Determination

The molecular weight distribution of the linear or substantially linear olefin interpolymer product samples is analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3, 10^4, 10^5, and 10^6), operating at a system temperature of 140° C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 200 microliters. A differential refractometer is being used as the detector.

The molecular weight determination 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 Word in *Journal of Polymer Science*, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) 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 according to the following formula: $M_w=\Sigma w_i*M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i^{th} fraction eluting from the GPC column.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin polymers, the molecular weight distribution (M_w/M_n) is preferably from about 1.8 to about 2.8, more preferably from about 1.89 to about 2.2 and especially about 2.

Determination of the Slope of Strain Hardening Coefficient

The slope of strain hardening is measured by compression molding a plaque from the polymer to be tested. Typically, the plaque is molded at about 177° C. for 4 minutes under almost no pressure and then pressed for 3 minutes under a pressure of about 200 psi. The plaque is then allowed to cool at about 8° C./minute while still under 200 psi pressure. The molded plaque has a thickness of about 0.005 inches. The plaque is then cut into a dogbone shaped test piece using a steel rule die. The test piece is 0.315 inches wide and 1.063 inches long. The start of the curved portion of the dogbone shape begins at 0.315 inches from each end of the sample and gently curves (i.e., tapers) to a width of 0.09 inches. The curve ends at a point 0.118 inches from the start of the curve such that the interior portion of the dogbone test piece has a width of 0.09 inches and a length of 0.197 inches.

The tensile properties of the test sample is tested on an Instron Tensile Tester at a crosshead speed of 1 inch/minute. The slope of strain hardening is calculated from the resulting tensile curve by drawing a line parallel to the strain hardening region of the resulting stress/strain curve. The strain hardening region occurs after the sample has pulled its initial load ((i.e., stress) usually with little or no elongation during the initial load) and after the sample has gone through a slight drawing stage (usually with little or no increase in load, but with increasing elongation (i.e., strain)). In the strain hardening region, the load and the elongation of the sample both continue to increase. The load increases in the strain hardening region at a much lower rate than during the initial load region and the elongation also increase, again at a rate lower than that experienced in the drawing region. FIG. **1** shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined.

The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

$$SHC=(slope\ of\ strain\ hardening)^*(I_2)^{0.25}$$

where I_2=melt index in grams/10 minutes.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers used in the invention, the SHC is greater than about 1.3, preferably greater than about 1.5.

Surprisingly, the slope of strain hardening coefficient reaches a maximum for the linear or the substantially linear ethylene/α-olefin polymers at a density from about 0.89 g/cm^3 to about 0.935 g/cm^3. Heterogeneous ethylene/α-olefin polymers, in contrast, do not behave in the same manner. FIG. **1** graphically depicts the relationship between the density of the homogeneously branched substantially linear ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient, and includes a heterogeneously branched ethylene/1-octene copolymer (polymer W** in Table 1) for comparison purposes. Table 1 displays the data of FIG. **1** in tabular form:

TABLE 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0.8564	7.36	0.004
B	1.03	0.8698	7.46	0.45
C	0.57	0.873	7.22	0.54
D	1.01	0.8817	7.36	0.89
E	1.06	0.9018	7.61	1.84
F	2.61	0.9041	8.07	2.03
G	0.77	0.9047	9.01	1.57
H	9.82	0.9048	7.03	1.67
I	4.78	0.9077	7.18	2.08
J	3.13	0.9113	7.67	2.04
K	2.86	0.9139	7.87	2.27
L	1.08	0.9197	8.07	2.24
M	0.96	0.9198	9.61	1.93
N	0.99	0.9203	9.09	2.23
O	1.11	0.9204	10.15	1.59
P	1.06	0.9205	9.08	2.25
Q	1.12	0.9216	8.94	2.3
R	30.74	0.9217	6.27	2
S	31.58	0.94	6.02	0.24
T	0.97	0.9512	12.11	0
U	0.97	0.9533	10.5	0
V	0.92	0.954	7.39	0
W**	0.8	0.905	8.7	1.02

*SHC = Slope of Strain Hardening Coefficient
**A comparative heterogeneously branched ethylene/1-octene copolymer

The Heterogeneously Branched Ethylene Polymer

The ethylene polymer to be combined with the homogeneous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer of ethylene with at least one C_3–C_{20} α-olefin (e.g., linear low density polyethylene (LLDPE)).

Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution. For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene). The amount of each of these fractions varies depending upon the whole polymer properties desired. For example, linear homopolymer polyethylene has neither branched nor highly branched fractions, but is linear. A very low density heterogeneous polyethylene having a density from about 0.9 g/cm^3 to about 0.915 g/cm^3 (such as Attane® copolymers, sold by The Dow Chemical Company and Flexomer® sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer.

Heterogeneously branched LLDPE (such as Dowlex® sold by The Dow Chemical Company) has a lower amount of the highly branched fraction, but has a greater amount of the medium branched fraction. FIG. 2 graphically depicts the relative amounts of these various fractions (as measured using temperature rising elution fractionation) for Dowlex® 2045 (a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.93 and a molecular weight distribution (M_w/M_n) of about 3.34), as compared with a homogeneously branched substantially linear ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10.5 and a molecular weight distribution (M_w/M_n) of about 2.18. Note that the homogeneously branched polymer has a single relatively narrow peak at an elution temperature of about 85° C., while the Dowlex® 2045 polymer has a broad branching distribution, as represented by the breadth of elution temperatures over which the polymer fractions elute. Dowlex® 2045 also has a distinct peak at an elution temperature of about 98° C., indicating the "linear" fraction of the whole polymer. Increasing the fraction of the polymer which has the beneficial properties, without concomitantly increasing other fractions has not been demonstrated here-to-fore.

Preferably, however, the heterogeneously branched ethylene polymer is a heterogeneously branched Ziegler polymerized ethylene/α-olefin interpolymer having no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1.3.

More preferably, the heterogeneously branched ethylene polymer is a copolymer of ethylene with a C_3–C_{20} α-olefin, wherein the copolymer has:

(i) a density from about 0.93 g/cm^3 to about 0.965 g/cm^3,

(ii) a melt index (I_2) from about 0.1 g/10 min to about 500 g/10 min, and

(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1.3.

The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC).

The Formulated Compositions

The compositions disclosed herein can be formed by any convenient method, including dry blending the individual components and subsequently melt mixing or by pre-melt mixing in a separate extruder (e.g., a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a twin screw extruder).

Another technique for making the compositions in-situ is disclosed in pending U.S. Ser. No. 08/010,958, now abandoned entitled Ethylene Interpolymerizations, which was filed Jan. 29, 1993 in the names of Brian W. S. Kolthammer and Robert S. Cardwell, the disclosure of which is incorporated herein in its entirety by reference. U.S. Ser. No. 08/010,958 now abandoned describes, inter alia, interpolymerizations of ethylene and C_3–C_{20} alpha-olefins using a homogeneous catalyst in at least one reactor and a heterogeneous catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel.

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i.e., branching) distribution, selecting the fraction having the specified properties (e.g., SHC≧1.3), and blending the selected fraction in the appropriate amounts with another ethylene polymer. This method is obviously not as economical as the in-situ interpolymerizations of U.S. Ser. No. 08/010,958, but can be used to obtain the compositions of the invention.

Fabricated Articles Made from the Novel Compositions

Many useful fabricated articles benefit from the novel compositions disclosed herein. For example, molding operations can be used to form useful fabricated articles or parts from the compositions disclosed herein, including various injection molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264–268, "Introduction to Injection Molding" by H. Randall Parker and on pp. 270–271, "Injection Molding Thermoplastics" by Michael W. Green, the disclosures of which are incorporated herein by reference) and blow molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume

65, Number 11, pp. 217–218, "Extrusion-Blow Molding" by Christopher Irwin, the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion (e.g., pipes) and the like. Rotomolded articles can also benefit from the novel compositions described herein. Rotomolding techniques are well known to those skilled in the art and include, for example, those described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 296–301, "Rotational Molding" by R. L. Fair, the disclosure of which is incorporated herein by reference).

Fibers (e.g., staple fibers, melt blown fibers or spunbonded fibers (using, e.g., systems as disclosed in U.S. Pat. No. 4,340,563, U.S. Pat. No. 4,663,220, U.S. Pat. No. 4,668,566, or U.S. Pat. No. 4,322,027, all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in U.S. Pat. No. 4,413,110, incorporated herein by reference)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in U.S. Pat. No. 3,485,706, incorporated herein by reference) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton)) can also be made from the novel compositions disclosed herein.

Film and film structures particularly benefit from the novel compositions described herein and can be made using conventional hot blown film fabrication techniques or other biaxial orientation processes such as tenter frames or double bubble processes. Conventional hot blown film processes are described, for example, in *The Encyclopedia of Chemical Technology*, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416–417 and Vol. 18, pp. 191–192, the disclosures of which are incorporated herein by reference. Biaxial orientation film manufacturing process such as described in a "double bubble" process as in U.S. Pat. No. 3,456,044 (Pahlke), and the processes described in U.S. Pat. No. 4,352,849 (Mueller), U.S. Pat. No. 4,597,920 (Golike), U.S. Pat. No. 4,820,557 (Warren), U.S. Pat. No. 4,837,084 (Warren), U.S. Pat. No. 4,865,902 (Golike et al.), U.S. Pat. No. 4,927,708 (Herran et al.), U.S. Pat. No. 4,952,451 (Mueller), U.S. Pat. No. 4,963,419 (Lustig et al.), and U.S. Pat. No. 5,059,481 (Lustig et al.), the disclosures of each of which are incorporated herein by reference, can also be used to make film structures from the novel compositions described herein. The film structures can also be made as described in a tenter-frame technique, such as that used for oriented polypropylene.

Other multi-layer film manufacturing techniques for food packaging applications are described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991), pp. 19–27, and in "Coextrusion Basics" by Thomas I. Butler, *Film Extrusion Manual: Process, Materials, Properties* pp. 31–80 (published by TAPPI Press (1992)) the disclosures of which are incorporated herein by reference.

The films may be monolayer or multilayer films. The film made from the novel compositions can also be coextruded with the other layer(s) or the film can be laminated onto another layer(s) in a secondary operation, such as that described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991) or that described in "Coextrusion For Barrier Packaging" by W. J. Schrenk and C. R. Finch, *Society of Plastics Engineers RETEC Proceedings*, Jun. 15–17 (1981), pp. 211–229, the disclosure of which is incorporated herein by reference. If a monolayer film is produced via tubular film (i.e., blown film techniques) or flat die (i.e., cast film) as described by K. R. Osborn and W. A. Jenkins in "Plastic Films, Technology and Packaging Applications" (Technomic Publishing Co., Inc. (1992)), the disclosure of which is incorporated herein by reference, then the film must go through an additional post-extrusion step of adhesive or extrusion lamination to other packaging material layers to form a multilayer structure. If the film is a coextrusion of two or more layers (also described by Osborn and Jenkins), the film may still be laminated to additional layers of packaging materials, depending on the other physical requirements of the final film. "Laminations Vs. Coextrusion" by D. Dumbleton (Converting Magazine (September 1992), the disclosure of which is incorporated herein by reference, also discusses lamination versus coextrusion. Monolayer and coextruded films can also go through other post extrusion techniques, such as a biaxial orientation process.

Extrusion coating is yet another technique for producing multilayer film structures using the novel compositions described herein. The novel compositions comprise at least one layer of the film structure. Similar to cast film, extrusion coating is a flat die technique. A sealant can be extrusion coated onto a substrate either in the form of a monolayer or a coextruded extrudate.

Generally for a multilayer film structure, the novel compositions described herein comprise at least one layer of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same film structure. Some of these materials include: foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic add (EAA) copolymers, ethylene/methacrylic add (EMAA) copolymers, LLDPE, HDPE, LDPE, nylon, graft adhesive polymers (e.g., maleic anhydride grafted polyethylene), and paper. Generally, the multilayer film structures comprise from 2 to about 7 layers.

EXAMPLE 1

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.91 g/cm^3, I_{10}/I_2 of about 10, M_w/M_n of about 2, and SHC of about 1.81 is dry blended and then melt blended with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC$\cong$1.3. The dry blend is tumble blended in a 50 gallon drum for about 1 hour.

The melt blend is produced in a ZSK 30 twin screw extruder (30 mm screw diameter) and is then fabricated into film. The final blended composition has a density of about 0.919 g/cm^3.

The blended composition is then fabricated into blown film having a thickness of about 1 mil on an Egan Blown Film Line having a 2 inch diameter screw, a 3 inch die and at a 2.5 inch blow up ratio (BUR), as described in Table 2. For all film samples in Examples 1, 2, 4, and 6 and for comparative examples 3, 5, and 7, the targeted gauge is about 1 mil, using a blow-up ratio (BUR) of 2.5:1, a LLDPE screw design is used, a die gap of 70 mils is used, and a lay flat of about 11.875 inches is used.

Film properties are measured and reported in Table 3 with other examples of the invention and with comparative

examples. Dart impact (type A) of the films is measured in accordance with ASTM D-1709-85; tensile strength, yield, toughness, and 2% secant modulus of the films is measured in accordance with ASTM D-882; Elmendorf tear (type B) is measured in accordance with ASTM D-1922; PPT tear is measured in accordance with ASTM D-2582; Block is measured in accordance with ASTM D-3354.

Puncture is measured by using an Instron tensiometer Tensile Tester with an integrator, a specimen holder that holds the film sample taut across a circular opening, and a rod-like puncturing device with a rounded tip (ball) which is attached to the cross-head of the Instron and impinges perpendicularly onto the film sample. The Instron is set to obtain a crosshead speed of 10 inches/minute and a chart speed (if used) of 10 inches/minute. Load range of 50% of the load cell capacity (100 lb. load for these tests) should be used. The puncturing device is installed to the Instron such that the clamping unit is attached to the lower mount and the ball is attached to the upper mount on the crosshead. Six film specimens are used (each 6 inches square). The specimen is clamped in the film holder and the film holder is secured to the mounting bracket. The crosshead travel is set and continues until the specimen breaks. Puncture resistance is defined as the energy to puncture divided by the volume of the film under test. Puncture resistance (PR) is calculated as follows:

$$PR=E/((12)(T)(A))$$

where

PR=puncture resistance (ft-lbs/in^3)

E=energy (inch-lbs)=area under the load displacement curve

12=inches/foot

T=film thickness (inches), and

A=area of the film sample in the clamp=12.56 in^2.

EXAMPLE 2

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 0.5 g/10 min, density of about 0.915 g/cm^3, I_{10}/I_2 of about 11, M_w/M_n of about 24, and SHC of about 2.265 is dry blended and then melt blended (as described in Example 1) with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The final blended composition has a density of about 0.92 g/cm^3.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

COMPARATIVE EXAMPLE 3

A heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.92 g/cm^3, I_{10}/I_2 of about 7.93, and M_w/M_n of about 3.34 is made into film as described in Example 1. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 36 percent (by weight of the heterogeneous copolymer) having a SHC≧1.3. The entire heterogeneous ethylene/1-octene copolymer has a SHC of about 1.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

EXAMPLE 4

Example 4 is an in-situ blend made according to U.S. Ser. No. 08/010,958, now abandoned wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a melt index (I_2) of about 0.5 g/10 min., and a density of about 0.9054 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8.27 and a molecular weight distribution (M_w/M_n) of about 1.979 and comprises about 50% (by weight of the total composition). A heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 1.5 g/10 min., and a density of about 0.944 g/cm^3 and comprises the remaining 50% (by weight of the total composition). The total composition has a melt index (I_2) of about 1 g/10 min., a density of about 0.9248 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.22 and a molecular weight distribution (M_w/M_n) of about 2.641. This composition is made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 5

Comparative Example 5 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, now U.S. Pat. No. 5,250,612 the disclosure of which is incorporated herein by reference. About 15% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.56 g/10 min., a density of about 0.9256 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 9.5 and a molecular weight distribution (M_w/M_n) of about 4.35. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

EXAMPLE 6

Example 6 is an in-situ blend made according to U.S. Ser. No. 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/l-octene copolymer having a fractional melt index (I_2), a density of about 0.906 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8–10 and a molecular weight distribution (M_w/M_n) of about 2.2 and comprises about 43% (by weight of the total composition). A second heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 0.85 g/10 minutes, a density of about 0.938 g/cm^3 and comprises the remaining 57% (by weight of the total composition). The total composition has a melt index (I_2) of about 0.53 g/10 minutes, a density of about 0.9246 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.83, and a molecular weight distribution (M_w/M_n) of about 2.8. This composition is made into blown film as described in Table 2 and the film properties are reported in Table 3.

COMPARATIVE EXAMPLE 7

Comparative Example 7 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, now U.S. Pat. No. 5,250,612 the disclosure of which is incorporated herein by reference. About 25% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.49 g/10 min., a density of about 0.9244 g/cm^3,

a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4.78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 8

Comparative example 8 is a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 minutes, a density of about 0.9249 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8 and a molecular weight distribution (M_w/M_n) of about 3.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and comparative examples.

TABLE 2

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Zone 1A (°F.)	300	300	300	300	300	300	300	300
Zone 1B (°F.)	450	451	475	474	475	475	475	474
Zone 1C (°F.)	450	450	475	475	475	475	475	475
Zone 2A (°F.)	450	450	475	474	475	475	475	475
Zone 2B (°F.)	450	450	455	475	475	475	475	475
Zone 2C (°F.)	450	450	475	475	475	475	475	475
Zone 3 (°F.)	451	452	474	477	477	476	476	474
Zone 4 (°F.)	450	450	473	475	475	475	475	475
Zone 5 (°F.)	450	450	475	475	475	475	475	475
Melt temp. (°F.)	475	477	515	501	502	499	499	497
Blower Air temp. (°F.)	47.3	45.7	57	44.4	86.5	47.6	NA	473
Chill Water temp. (°F.)	39	37.6	51.1	38.3	86.8	40	38.7	40.5
Extruder Die press. (psi)	2843	3427	1321	1874	1763	2883	2525	1952
Nozzle press (in.)	3.2	4.5	4.38	4.4	4.9	4.6	4.6	4.3
Amps	27.3	33.1	37.7	39.9	40.2	50.1	42.6	38.6
Extruder speed (rpm)	27.6	28.8	21.5	23.1	21.1	21.5	22.1	21.7
Nip Roll speed (rpm)	33.1	36.9	39	39.8	36.2	37	36	37.8
Output (lbs/hr)	31	NR*	38.3	39	NR*	36	36	36
Frostline height (in.)	12.5	9	13	12	12	10.5	11	10.5

*NR = Not recorded

TABLE 3

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Yield (MD*) (psi)	1605	1595	1643	2040	2243	1973	1810	1782
Tensile (MD*) (psi)	8522	9525	7444	7794	7931	9325	8455	4928
Toughness (MD*) (ft-lbs/in^3)	1689	1773	1439	1671	1519	NR	NR	NR
Yield (CD**) (psi)	1530	1489	1706	2267	2407	1997	1809	1832
Tensile (CD**) (psi)	6252	7603	5807	7079	7458	7153	6326	4598
Toughness (CD**) (ft-lbs/in^3)	1282	1599	1358	1656	1495	NR	NR	NR
Elmendorf B (MD*) (grams)	288	216	334	317	194	320	398	297
Elmendorf B (CD**) (grams)	621	566	413	630	664	640	621	527
PPT Tear (MD*) (lbs.)	6.79	6.18	5.99	6.2	6.5	6.2	6.2	5.3
PPT Tear (CD**) (lbs.)	7.44	7.42	6.46	6.8	8.1	7.0	7.5	6.1
Dart Impact A (grams)	708	610	354	410	186	412	186	164
Puncture (ft-lbs/in^3)	316	349	251	231	256	250	227	237
Film Block g.	75	33	87	32	17	11.8	17	22
Film Gradient Density (g/cm^3)	0.9145	0.9153	0.9155	0.9205	0.9218	0.9198	0.9201	0.9207
Film Gauge (low) (mils)	0.9	0.9	0.9	0.85	0.8	0.98	0.95	1.05
Film Gauge (high) (mils)	1.2	1.05	1.1	0.95	1	1.08	1.05	1.15

*MD = Machine direction
**CD = Cross direction
NR = Not Recorded

In general, films made from the novel formulated ethylene/α-olefin compositions exhibit good impact and tensile properties, and an especially good combination of tensile, yield and toughness (e.g., toughness and dart impact). Further, films from the example resins exhibited significant improvements over films made from the comparative resins in a number of key properties.

For example, comparing examples 1 and 2 with comparative example 3, the data show films produced from the melt blends (examples 1 and 2) exhibited significantly higher values for the following film properties: dart impact, MD tensile, CD tensile, MD toughness, CD toughness MD ppt tear, CD ppt tear, CD Elmendorf tear B, puncture and significantly lower block.

Comparing example 4 to comparative example 5, the data show films produced from the in-situ blend (made according to U.S. Ser. No. 08/010,958 now abandoned) exhibited significantly higher values for the following film properties: dart impact, MD toughness and CD toughness.

Comparing example 6 to comparative examples 7 (an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375 now U.S. Pat. No. 5,250,612) and 8 (an heterogeneously branched ethylene/1-octene copolymer), the data show films produced from the in-situ blend (made according to U.S. Ser. No. 08/010,958) exhibited significantly higher values for the following film properties: dart impact, MD yield, CD yield, MD tensile, CD tensile, CD Elmendorf tear B and puncture and significantly lower block.

We claim:

1. A film made from an ethylene polymer composition, wherein the composition comprises (A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.935 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry, and

(vi) a slope of strain hardening coefficient greater than or equal to 1.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched linear ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

2. The film of claim **1** wherein the homogeneously branched linear ethylene interpolymer has a slope of strain hardening coefficient greater than or equal to 1.5.

3. The film of claim **1** wherein the homogeneously branched linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

4. The film of claim **1** wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

5. The film of claim **4** wherein the homogeneously branched linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

6. An ethylene polymer composition comprising (A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.935 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry, and

(vi) a slope of strain hardening coefficient greater than or equal to 1.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched linear ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

7. The composition of claim **6** wherein the homogeneously branched linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to 1.5.

8. The composition of claim **6** wherein the homogeneously branched linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

9. The composition of claim **6** wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

10. The composition of claim **9** wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and 1-octene.

11. The composition of claim **6** wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

12. The composition of claim **11** wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

13. The film of claim **9** or the composition of claim **6**, wherein the density of the at least one homogeneously branched linear ethylene/α-olefin interpolymer is in the range from about 0.905 g/cm^3 to about 0.925 g/cm^3 and the I_2 melt index is in the range of from about 0.001 g/10 minutes to less than about 1 g/10 minutes.

14. The film of claim **1** wherein the heterogeneously branched linear ethylene polymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

15. The film of claim **14** wherein the heterogeneously branched linear ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

16. The film of claim **15** wherein the heterogeneously branched linear ethylene polymer is a copolymer of ethylene and 1-octene.

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