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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
08/927,393	08/27/97	CHUM	P 40121BU

IM22/0930

THE DOW CHEMICAL COMPANY
B-1211 PATENT DEPT
FREEPORT TX 77541

EXAMINER	
HARLAN,R	
ART UNIT	**PAPER NUMBER**
1713	8

DATE MAILED: 09/30/99

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

PTO-90C (Rev. 2/95)

1- File Copy

Office Action Summary	Application No. 08/927,393	Applicant(s) Chum, et al.
	Examiner Robert D. Harlan	Group Art Unit 1713

☐ Responsive to communication(s) filed on _____.

☐ This action is **FINAL**.

☐ Since this application is in condition for allowance except for formal matters, **prosecution as to the merits is closed** in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11; 453 O.G. 213.

A shortened statutory period for response to this action is set to expire 3 month(s), or thirty days, whichever is longer, from the mailing date of this communication. Failure to respond within the period for response will cause the application to become abandoned. (35 U.S.C. § 133). Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

Disposition of Claims

☒ Claim(s) *36-51* is/are pending in the application.

Of the above, claim(s) _____ is/are withdrawn from consideration.

☐ Claim(s) _____ is/are allowed.

☒ Claim(s) *36-51* is/are rejected.

☐ Claim(s) _____ is/are objected to.

☐ Claims _____ are subject to restriction or election requirement.

Application Papers

☒ See the attached Notice of Draftsperson's Patent Drawing Review, PTO-948.

☐ The drawing(s) filed on _____ is/are objected to by the Examiner.

☐ The proposed drawing correction, filed on _____ is ☐ approved ☐ disapproved.

☐ The specification is objected to by the Examiner.

☐ The oath or declaration is objected to by the Examiner.

Priority under 35 U.S.C. § 119

☐ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☐ All ☐ Some* ☐ None of the CERTIFIED copies of the priority documents have been

☐ received.

☐ received in Application No. (Series Code/Serial Number) _____.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

*Certified copies not received: _____.

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

Attachment(s)

☒ Notice of References Cited, PTO-892

☐ Information Disclosure Statement(s), PTO-1449, Paper No(s). _____

☐ Interview Summary, PTO-413

☒ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

--- *SEE OFFICE ACTION ON THE FOLLOWING PAGES* ---

DETAILED ACTION

Claim Rejections - 35 USC § 102 and § 103

1. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless --
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

2. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

3. Claims 36-51 are rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over WO 90/03414 (hereinafter "WO '414).

4. In examples 1 and 2, and Table 1, WO '414 discloses polymer blends B1 and B2 made by ethylene polymers '006 and '013 wherein the CBDI, melt index, and density fail into the same ranges as claimed. Although WO '414 fails to show the value of the slope of strain hardening coefficient of polymer '013 and a temperature rising elution fractionation (TREF) showing a

linear polymer portion of '006, in view of other substantially similar physical properties and processes for making the ethylene polymer, the examiner has a reasonable basis to believe that it inherently possesses said slope of strain hardening coefficient and said linear polymer portion. The polymer blends of WO '414 are not necessarily different from the claimed polymer blends. Since the examiner does not have proper equipment to carry out of the analytical tests, the burden is on the applicant to prove the claimed polymer blends are necessarily different from those of WO' 414 and unobvious thereof. In re Fitzgerald et al., 205 USPQ 594 (CCPA 1980).

5. Even if the properties of polymer composition of the instant claim and the prior art examples are not the same, it would still have been obvious to one of ordinary skill in the art to make polymers having the claimed properties because it appears that the reference generically embrace the claimed polymer blends and the person of ordinary skill in the art would have expected all embodiments of the reference to work. Applicants have not demonstrated that the difference, if any, between the claimed product and the products of the prior art examples give rise to unexpected results.

6. The Markovich declaration filed on 27 Aug. 1997 has been considered but deemed not to be persuasive since the comparative test do not show unexpected results of the claimed polymer blends. In the 28/50/72 blends the toughness properties of the comparative runs is not

necessarily inferior to that of the inventive runs. Since applicants have not met their burden to provide objective evidence demonstrating the claimed polymer blends are in fact different from those of WO '414, the 102(b)/103 rejection is still deemed to be proper.

Double Patenting

7. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. See *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970);and, *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321© may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the conflicting application or patent is shown to be commonly owned with this application. See 37 CFR 1.130(b).

Effective January 1, 1994, a registered attorney or agent of record may sign a terminal disclaimer. A terminal disclaimer signed by the assignee must fully comply with 37 CFR 3.73(b).

8. Claim 36-51 are rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-18 of U.S. Patent No. 5,677,383 (hereinafter the "Chum patent"). Although the conflicting claims are not identical, they are not patentably distinct from each other because the claims of the instant invention are generic in scope referring to "ethylene interpolymer" and "ethylene polymer" while the claims of the Chum patent are restricted to a species (i.e. "homogeneously branched substantially linear ethylene/olefin interpolymer." "heterogeneously branched ethylene polymer") of the generic claim. The PTO

may reject the generic claims on the grounds of obvious-type double patenting. See In re Braithwaite, 379 F.2d 594, USPQ 29 (CCPA 1967); see also MPEP 806.04(I)

9. The subject matter claimed in the instant application is fully disclosed and claimed by the Chum patent. Furthermore, there is no apparent reason why applicant was prevented from presenting claims corresponding to those of the instant invention during prosecution of the application which matured into a patent. See In re Schneller, 397 F.2d 350, 158 USPQ 210 (CCPA 1968); see also MPEP 804.

Conclusion

10. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Robert D. Harlan whose telephone number is (703)306-5926. The examiner can normally be reached on weekdays from 9 am to 6 pm.

11. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, David Wu, can be reached on (703)308-2450. The fax phone number for the organization where this application or proceeding is assigned is (703)306-3429.

Robert Harlan

DAVID W. WU
PRIMARY EXAMINER
GROUP 1800

Notice of References Cited

Application No.	Applicant(s)		
08/927,393	Chum, et al.		
Examiner		Group Art Unit	Page 1 of 1
Robert D. Harlan		1713	

U.S. PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS
X	A	5,677,383	10/14/97	Chum, et al.	525	240
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUBCLASS
X	N	WO 90/03414	09/28/89	PCT	Stehling, et al.	525	--
	O						
	P						
	Q						
	R						
	S						
	T						

NON-PATENT DOCUMENTS

*		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
	U		
	V		
	W		
	X		

* A copy of this reference is not being furnished with this Office action. (See Manual of Patent Examining Procedure, Section 707.05(a).)

US005677383A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,677,383

[45] Date of Patent: Oct. 14, 1997

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

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

[21] Appl. No.: **544,497**

[22] Filed: **Oct. 18, 1995**

Related U.S. Application Data

[63] 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 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320

[56] **References Cited**

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(List continued on next page.)

Primary Examiner—David W. Wu

[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.

18 Claims, 2 Drawing Sheets

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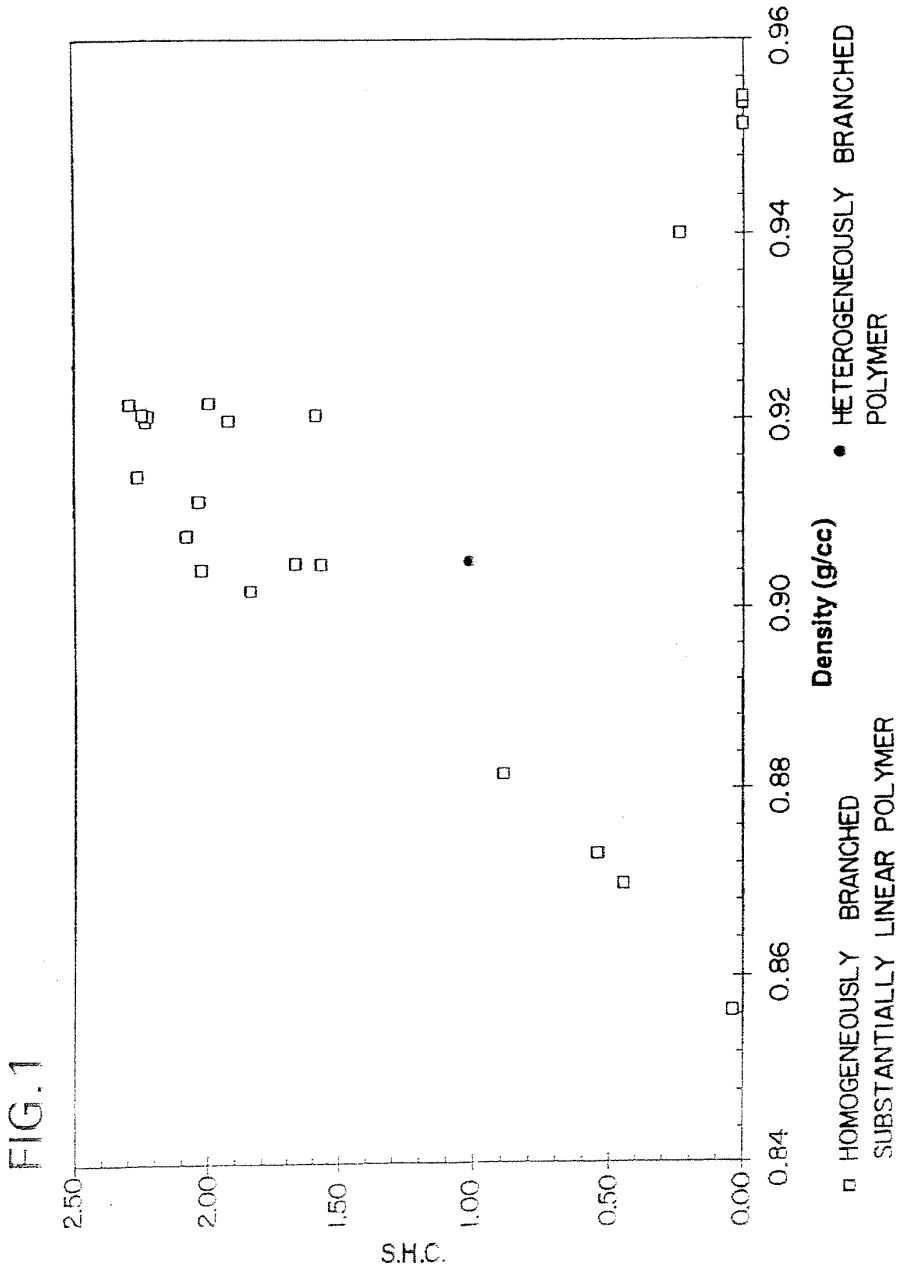

0.96
0.94
0.92
0.90
0.88
0.86
0.84
Density (g/cc)
2.50
2.00
1.50
1.00
0.50
0.00
S.H.C.
HETEROGENEOUSLY BRANCHED POLYMER
HOMOGENEOUSLY BRANCHED SUBSTANTIALLY LINEAR POLYMER

FIG. 1

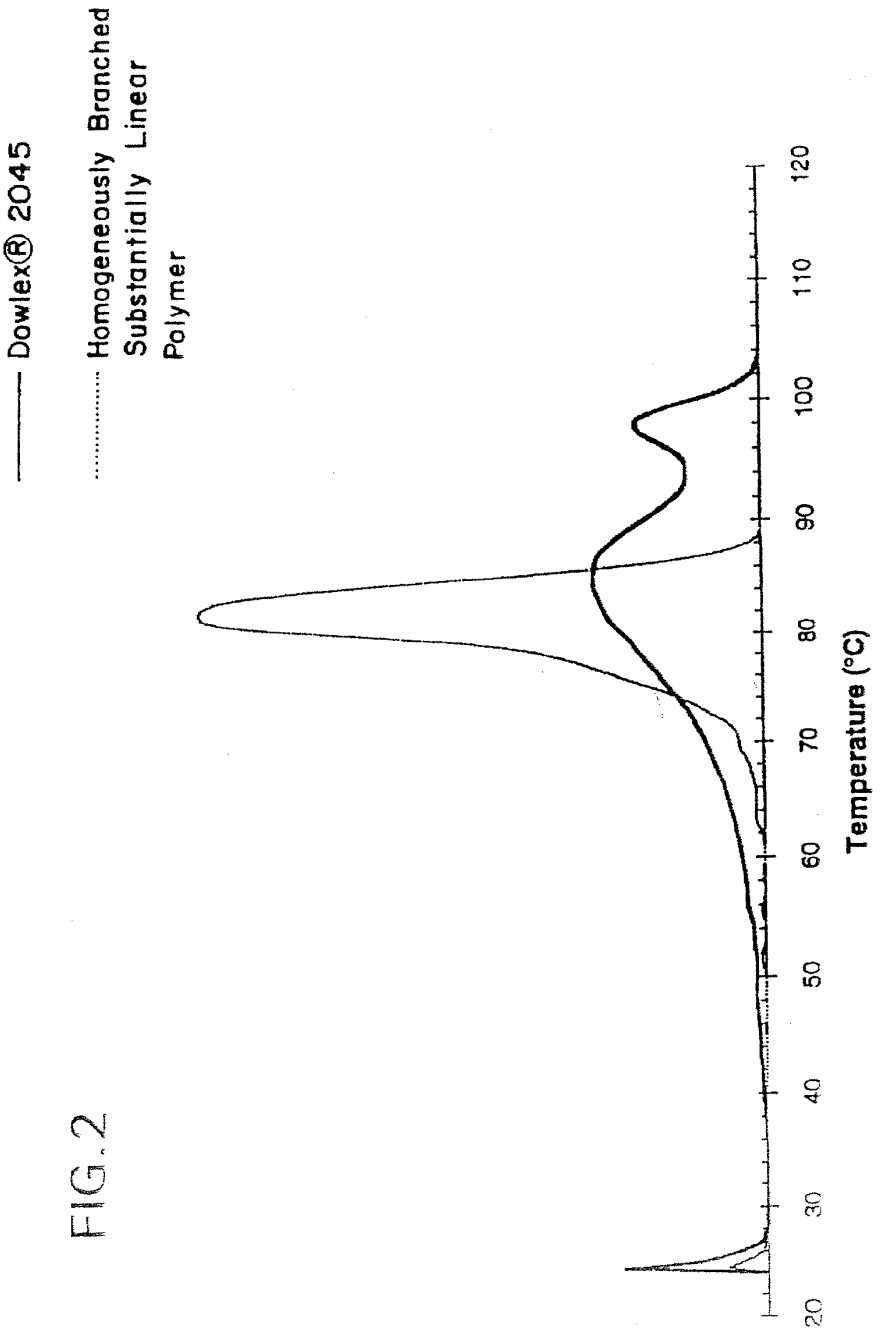

Dowlex® 2045
Homogeneously Branched Substantially Linear Polymer
Temperature (°C)
20
30
40
50
60
70
80
90
100
110
120

FIG. 2

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Rule 1.60 continuation application of application No. 08/378,998, filed Jan. 27, 1995, now abandoned, which was a Rule 1.62 continuation application of application No. 08/054,379, filed Apr. 28, 1993, now abandoned, which was a continuation-in-part application of 07/776,130, filed Oct. 15, 1991, now issued U.S. Pat. No. 5,272,236, the disclosures of each of which is incorporated herein in their entirety by reference. This application is also related to application number 08/501,527, filed Aug. 2, 1995, now U.S. Pat. No. 5,609,242 which is a continuation of 08/010,958, filed Jan. 29, 1993, now abandoned, the disclosure of which is 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 homogeneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.5.

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 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 150° C. 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 Critical Shear Stress and Critical Shear Rate

Gas extrusion rheometry (GER) is described by M. Shida, R. N. Shroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97, both publications of which are incorporated by reference herein in their entirety. All GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die. An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in *Journal of Rheology*, 30(2), 337–357 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40× magnification. The critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably, the critical shear stress at the OGMF and the critical shear stress at the OSMF for the substantially linear ethylene polymers used herein is greater than about 4×10^6 dyne/cm^2 and greater than about 2.8×10^6 dyne/cm^2, respectively.

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:

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

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	2.01	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	0.9115	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, now abandoned 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. Nos. 4,340,563, 4,663,220, 4,668,566, or 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 acid (EAA) copolymers, ethylene/methacrylic acid (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≧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 2.4, 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 now abandoned, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-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	47.5	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	47.3
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	2893	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
Frost line 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	2,50	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 shows 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 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 high density fraction,

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

(vi) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; 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 ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to 1.3.

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

3. The film of claim 2 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

4. The film of claim 3 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

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

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

7. The film of claim 6 wherein the homogeneously branched substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

8. In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition 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 high density fraction,

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

(vi) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 $dyne/cm^2$, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; and

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 ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to 1.3.

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

10. The improvement of claim 8 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

11. The improvement of claim 10 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and 1-octene.

12. The improvement of claim 8 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

13. The improvement of claim 12 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

14. 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 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/min.,

(iv) no high density fraction,

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

(vi) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 $dyne/cm^2$, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; 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 ethylene polymer.

15. 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 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/min.,

(iv) no high density fraction,

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

(vi) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 $dyne/cm^2$, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; 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 ethylene polymer.

16. 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 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 high density fraction,

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

(vi) a critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; 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 ethylene polymer.

17. 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 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 high density fraction,

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

(vi) a critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and

(vii) a slope of strain hardening coefficient from 1.3 to 2.3; 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 ethylene polymer.

18. The film of claims **14** or **16**, or the composition of claims **15** or **17**, wherein the composition comprises more than about 40 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer.

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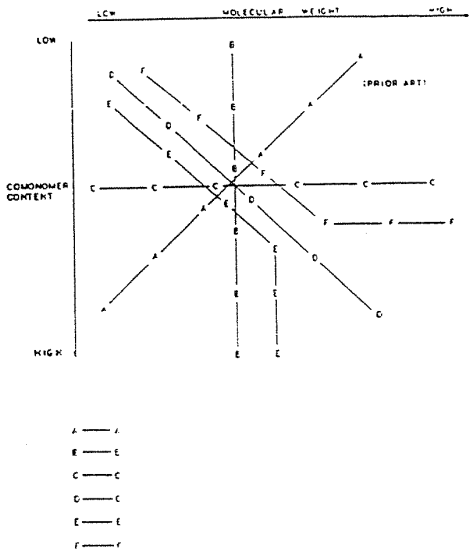
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(54) Title: LINEAR ETHYLENE INTERPOLYMER BLENDS OF INTERPOLYMERS HAVING NARROW MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS

(57) Abstract

Linear ethylene interpolymer blends are disclosed. The blends are made from components having a narrow molecular weight distribution (e.g. $M_w/M_n \leq 3$) and a narrow composition distribution (e.g. CDBI > 50 %). The blend components in a blend can all have the same molecular weight but different comonomer contents, the same comonomer content but different molecular weights, or comonomer contents which increase with molecular weight. The blends have either $M_w/M_n > 3$ or CDBI < 50 %, or both, and can be multimodal with respect to either or both molecular weight and/or comonomer content. The blends are generally free of blend components having both a higher average molecular weight and a lower average comonomer content than another blend component. The blends can have improved mechanical, physical and/or chemical properties.



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LINEAR ETHYLENE INTERPOLYMER BLENDS OF INTERPOLYMERS HAVING NARROW MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS

SPECIFICATION

Field of the Invention

The present invention relates to polymer blends of crystalline interpolymers, such as LLDPE, and more particularly to blends of such interpolymers wherein each blend component has a narrow molecular weight distribution and a narrow composition distribution selected to obtain superior properties in the blend.

Background of the Invention

Various types of polyethylene are known in the art. Low density polyethylene ("LDPE") is generally prepared at high pressure using free radical initiators and typically has a density in the range of 0.915-0.940 g/cm^3. LDPE is also known as "branched" polyethylene because of the relatively large number of long chain branches extending from the main polymer backbone.

High density polyethylene ("HDPE") usually has a density in the range of greater than 0.940 to 0.960 g/cm^3. HDPE is prepared using a coordination catalyst, e.g. Ziegler-Natta type catalysts, at low or moderate pressures, but sometimes at high pressure. HDPE is

generally linear without any substantial side chain branching. HDPE is a substantially crystalline polymer.

Linear, low density polyethylene ("LLDPE") is generally prepared in the same manner as HDPE, but incorporates a relatively minor amount of an α-olefin comonomer such as butene, hexene or octene to introduce enough short chain branches into the otherwise linear polymer to reduce the density of the resultant polymer into the range of that of LDPE. The coordination catalysts used to interpolymerize ethylene and the α-olefin generally produce an LLDPE with a relatively broad weight molecular weight distribution, i.e., Mw/Mn greater than about 3. Such LLDPE's also have relatively broad composition distribution in that the proportion of α-olefin comonomer molecules incorporated into the polymer molecules varies. Generally, the lower molecular weight polymer molecules contain a relatively higher proportion of the α-olefin comonomer than the higher molecular weight polymer molecules.

A polyethylene such as LLDPE having a broad molecular weight distribution is undesirable in many respects, depending on the desired end use application. For example, LLDPE resins known in the prior art containing relatively high molecular weight molecules are subject to orientation which results in anisotropic properties in the machine versus transverse direction of a fabrication process. On the other hand, resins containing relatively lower molecular weight molecules, in which the comonomer is invariably concentrated, tend to exhibit high block and tackiness. These lower molecular weight, highly branched molecules interfere with the proper function of certain additives compounded in the resin, increase the percentage of extractable polymer, and increase fouling in the polymerization plant. The relatively high α-olefin comonomer content of these low molecular weight polymer molecules causes such polymer molecules to be generally

amorphous and to exude to the surface of fabricated parts, thereby producing an undesirable sticky surface.

Prior art polyethylenes such as LLDPE also generally tend to have a very broad, nonuniform distribution of comonomer content, i.e. some polymer molecules have a relatively high α-olefin comonomer content while others have a relatively low content. Generally, the polymer molecules of low comonomer content are relatively more crystalline and have a high melting temperature, whereas the high comonomer content polymer molecules are more amorphous and melt at a lower temperature. The presence of a higher melting component is disadvantageous in many applications, for example where softness or clarity is desired. On the other hand, the presence of a lower melting component frequently results in a high quantity of extractables, which limit food contact applications.

Prior art blends of polyethylenes designed to improve one or more of the properties of the blend relative to its blend components or prior art polyethylene have also suffered from the drawbacks mentioned above. For example, incorporating a blend component with a high average comonomer content to reduce crystallizability generally results in an increase of extractables and adversely affects other properties so that the full advantage of the blend is not realized. Thus, there is a need to provide ethylene interpolymer blends with superior properties and in which the full advantages of blending may be realized.

Summary of the Invention

The present invention provides a blend of ethylene interpolymer components with narrow molecular weight and composition distributions selected to obtain an overall molecular weight and composition distribution in the resulting blend to impart superior properties thereto. Broadly, the blends of this invention comprise a plurality of linear ethylene interpolymer components wherein each component has a M_w/M_n value less than or equal to 3 and a composition distribution breadth index (as later

described) of 50% or higher. The blend is substantially free of blend components having both a higher average molecular weight and a lower average comonomer content than that of any other polyethylene component in the blend. The components for the blend can be selected so that the resultant blend has plural modality with respect to molecular weight distribution, comonomer content, or both.

In another aspect, the components for the blend are linear ethylene interpolymers having the narrow molecular weight and composition distributions mentioned above and the blend components are selected from one of the groups consisting of: (1) linear ethylene interpolymer blend components having substantially the same average molecular weight but different average comonomer contents; (2) linear ethylene interpolymer blend components having substantially the same average comonomer content but different average molecular weights; and (3) linear ethylene interpolymer blend components having different average molecular weights and comonomer contents in which the blend components, taken serially in order of increasing average molecular weight, have an increasing comonomer content.

In still another aspect, the linear ethylene interpolymer blend components have the narrow molecular weight and composition distribution mentioned above, and for the linear ethylene interpolymer blend components taken serially in order of increasing average molecular weight, then each succeeding component has substantially the same or a higher average comonomer content than each preceding component in said series.

In another aspect, the invention provides a linear ethylene interpolymer having plural modality with respect to comonomer content, a narrow molecular weight distribution such that $M_w/M_n \leq 3$ and an overall composition distribution breadth index less than 50%.

In still another aspect, the invention provides a linear ethylene interpolymer having plural modality with respect to molecular weight so that the blend has broad overall molecular weight distribution such that $M_w/M_n > 3$ and a composition distribution breadth index greater than or equal to 50%.

In still another aspect, the invention provides a linear ethylene interpolymer of plural modality with respect to both comonomer content and molecular weight, comprising a plurality of components having a narrow molecular weight distribution such that $M_w/M_n \leq 3$ for each fraction and each component taken serially in order of increasing average molecular weight, has an increasing average comonomer content.

In a still further aspect of the invention, there is provided a linear ethylene interpolymer blend of plural modality with respect to both comonomer content and molecular weight which comprises a plurality of components having a composition distribution breadth index of 50% or more, wherein the components taken serially in order of increasing comonomer content, have an increasing average molecular weight.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of different blends made from poly(ethylene-co-α-olefin) blend components having narrow molecular weight and composition distributions.

Fig. 2 illustrates the broad molecular weight distribution and broad composition distribution of a typical prior art LLDPE.

Fig. 3 illustrates the narrow molecular weight distribution and narrow composition distribution of an exemplary blend component used in the present invention.

Fig. 4 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to an embodiment of the invention in which the

blend components have about the same molecular weight but differing comonomer contents.

Fig. 5 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to another embodiment of the invention in which the blend components have about the same comonomer content but differing molecular weights.

Fig. 6 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to yet another embodiment of the invention in which the conomoner contents of the blend components increases as the molecular weight increases.

Description of the Preferred Embodiments

The linear ethylene interpolymer blend components in the present invention are higher interpolymers of a major proportion of ethylene and a minor proportion of comonomer. The ethylene is generally polymerized in a proportion of 70-100, typically 70-97, and often 70-80, 80-90 or 90-95, mole percent of the interpolymerized monomers with 0-30, typically 3-30, and often 20-30, 10-20 or 5-10, mole percent comonomer. Contemplated blend components generally include elastomer blend components in the density range of about 0.85-0.900 g/cm^3, very low density polyethylene blend components in the density range of about 0.900-0.915 g/cm^3, and linear, low density polyethylene blend components in the density range of about 0.915-0.940 g/cm^3. Ethylene interpolymers having a density in the high density polyethylene range above about 0.940 g/cm^3 are also contemplated as being suitably employed in the invention.

Suitable comonomers interpolymerized with the ethylene to obtain the ethylene interpolymer blend components herein generally include monomers which may be copolymerized with ethylene to obtain the molecular weight distribution and comonomer distribution desired in the blend component. A preferred class of comonomers are the

α-olefins having 3 to about 12 carbon atoms, such as propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecane and the like. Other suitable comonomers include vinyl cyclohexane, norbornene, vinyl cyclohexene, and other diene comonomers such as 1,3-butadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,5-hexadiene and the like. The ethylene interpolymer may include one or more of such comonomers, i.e. it may be a copolymer, terpolymer, etc.

The molecular weight of the LLDPE blend components may range from one thousand to one million or more depending on the particular end use, preferably 10^4-10^6, and especially $2 \times 10^4 - 5 \times 10^5$. As used herein, the terms "average molecular weight" and "molecular weight" refer to weight average molecular weight unless otherwise indicated. The linear polyethylene blend components preferably have a narrow molecular weight distribution (MWD). By "narrow MWD" is meant that the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n) is less than or equal to 3.0. Particularly preferred are the linear polyethylene blend components having a very narrow MWD, i.e. M_w/M_n less than or equal to 2.5, and especially less than or equal to 2.0. Molecular weight distributions of ethylene interpolymers are readily determined by techniques known in the art, such as, for example, size exclusion chromatography.

The linear polyethylene blend components preferably have a composition distribution (CD) such that the composition distribution breadth index (CDBI) is at least 50%. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%. The CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising

elution fractionation as described, for example, in U.S. Patent Application Serial No. 151,350 or in Wild et al., J. Poly. Sci, Poly. Phys. Ed., vol. 20, p. 441 (1982). Unless otherwise indicated, terms such as "comonomer content", "average comonomer content" and the like refer to the bulk comonomer content of the indicated interpolymer blend, blend component or fraction on a molar basis.

A graphical illustration of an exemplary narrow MWD, narrow CD blend component is seen in Fig. 3. In this three-dimensional figure, the Y-axis is the molecular weight, the X-axis is the molar comonomer content, and the Z-axis represents the incidence or weight proportion of molecules. As can be seen, the MWD and the CD of the blend component are narrow and appear as relatively sharp peaks in Fig. 3. In contrast, the MWD/CD diagram for a typical conventional LLDPE seen in Fig. 2 shows a broad MWD and a broad CD, and the comonomer content tends to decrease as the molecular weight increases.

In the blends of the present invention, one or more of the properties of the blend are improved by appropriate selection of narrow MWD, narrow CD blend components. In one embodiment, for example, tear strength may be controlled by blending linear polyethylene resins having about the same average molecular weight but with different average comonomer contents. Such a blend is illustrated as line B in Fig. 1. In another embodiment, the comonomer contents of the linear polyethylene blend components are the same, but molecular weights are varied, as illustrated by line C in Fig. 1. In still further embodiments illustrated by lines D, E and F in Fig. 1, the blend components taken serially in order of increasing molecular weight, or in order of increasing molar comonomer content, have the same or higher comonomer content or molecular weight, respectively.

As used herein, two or more blend components have substantially the same molecular weight if the resulting

MWD of the blend thereof is similarly narrow to the MWD of each blend component, i.e. the value of M_w/M_n of the resulting blend is less than or equal to about 3.0, preferably less than about 2.5. Conversely, two or more blend components have a different average molecular weight if the overall M_w/M_n of the resulting blend is relatively greater than for each such blend component, i.e., the M_w/M_n of the blend is greater than 3.0. As used herein, two or more blend components have a different comonomer content if the overall CDBI of the resulting blend is relatively less than that of each such blend component, i.e., the overall CDBI of the blend is less than 50%. Conversely, two or more blend components have substantially the same molar comonomer content if the resulting CD of the blend thereof is similarly narrow with respect to each blend component, i.e., the resulting blend has a CDBI of 50% or greater. It is readily appreciated that the CD and MWD of a blend can depend on the relative proportions of each blend component employed therein. It is specifically contemplated that blend components may have the "same" molecular weight for purposes of one blend, but not for the purpose of another blend, e.g. wherein the components would result in the blend having an MWD less than or greater than 3.0 depending on the proportion of each blend component. Similarly, blend components may have a "different" comonomer content for purposes of one blend, but not for the purposes of another blend, e.g. wherein the components would result in the final blend having CDBI less than or greater than 50% depending on the proportion of each blend component.

The molecular weight and composition distribution of a bimodal blend of the invention is illustrated graphically in Fig. 4. It is seen from this MWD/CD diagram that the comonomer content of each of the blend components is different, while the molecular weight of each blend component is about the same. This blend corresponds to line B of Fig. 1. In contrast, a similar

graph for typical conventional LLDPE is seen in Fig. 2, and line A of Fig. 1, and shows that the lower molecular weight fractions contain more of the comonomer than the higher molecular weight fractions. The lower molecular weight molecules which contain relatively high comonomer concentrations as in this conventional LLDPE can cause undesirable effects such as poor surface properties, high block and tackiness, cling development, high levels of extractables, and fouling of polymerization plants. In the present invention, such effects are minimized and properties are enhanced by providing blends of the type illustrated in Curve B, C, D, E, and F.

As an example of the embodiment of Curve B, it has been found that a 50-50 blend of a first LLDPE having a 6.4 mole% 1-butene content and a M_w of 80,400 (M_w/M_n = 2.3; CDBI = ~67%; MI 4.0 dg/min; density 0.9042 g/cm^3) with a HDPE having a 0.0 mole% 1-butene content and a M_w of 76,700 (M_w/M_n = 2.8; CDBI = ~100%; MI 5.0 dg/min; density 0.9552 g/cm^3) has an Elmendorf tear strength of 210 g/mil, synergistically enhanced in contrast to the tear strengths of 111 and 48 g/mil for the respective first and second blend components. Further, a 25-75 blend of these same components has a further enhanced Elmendorf tear strength of 227 g/mil. This result is quite surprising and unexpected because including a higher proportion of the second LLDPE resin with the lower tear strength in the blend increases the tear strength of the resulting blend, rather than decreasing the tear strength as would be expected.

In another embodiment exemplified in Fig. 5 and line C of Fig. 1, a multimodal MWD is obtained by blending linear polyethylene components having narrow molecular weight and composition distributions, and about the same comonomer content, but differing molecular weights. The molecular weight distribution of such blends improves the melt processability and rheological characteristics thereof, for example, high extrusion rates, high bubble

stability, high shear sensitivity, reduced draw resonance. On the other hand, the optical properties of mechanical, surface and individual blend components are generally substantially retained or improved in the blend thereof, including, for example tear strength, modulus, yield strength, reduced blocking, clarity, gloss, haze and the like. Moreover, such blends have lower portions of soluble molecules than prior art copolymers having similar molecular weight distribution. Desirable molecular weight and composition distributions may be obtained by blending different components, or by polymerization of the blend components simultaneously in the same reactor or in multiple reactors.

The higher molecular weight fraction containing relatively less comonomer as in conventional LLDPE may cause an anisotropic morphology during fabrication processing known as "row nucleated" or "shish-ka-bob" morphology. This anisotropic morphology is believed to contribute to poor toughness in articles crystallized from flowing melts. In the present invention, the anisotropy may be minimized by providing a blend with lower concentrations of such higher molecular weight molecules with a relatively low comonomer content and by incorporating the comonomer in the blend components as indicated in blend B, C, D, E and F.

In another embodiment as exemplified by Fig. 5 and line D of Fig. 1, the blend includes components having narrow molecular weight and composition distributions, but differing average molecular weights and average comonomer contents. However, in contrast to conventional LLDPE as illustrated in line A of Fig. 1 and in Fig. 2, the blend of this embodiment has a greater comonomer content in the higher molecular weight fractions or blend components than in the lower molecular weight fractions or blend components. These distributions are obtained, for example, by blending narrow MWD, narrow CD linear polyethylene resins which, taken serially in order of

increasing molecular weight, have an increasing comonomer content. It is also contemplated that the blend may include two or more blend components having the same molecular weight as illustrated by line F in Fig. 1, in which case such components would be included in the serial ordering secondarily in order of their increasing average comonomer content. Also, the presence of two or more blend components having the same comonomer content is also contemplated as being within the purview of this embodiment, as illustrated by line E in Fig. 1, provided that there is included either at least one blend component having a higher comonomer content and molecular weight or at least one blend component having a lower comonomer content and lower molecular weight than any of the blend components having the same comonomer content. In this embodiment, the blend is preferably substantially free of blend components having both a higher molecular weight and a lower comonomer content than any component present in the blend.

Such a blend has properties which are significantly different from prior art blends and conventional LLDPE resins in which the comonomer content generally decreases in proportion to increasing molecular weight components or fractions. The isotropy and toughness of films made from such blends are improved by minimizing the anisotropic shish-ka-bob or row-nucleated morphology ordinarily caused by a low concentration of comonomers present in the higher molecular weight molecules in conventional LLDPE resins. Moreover, such blends have desirable properties such as, for example, reduced blocking, reduced coefficients of friction, and lower extractables, in comparison to conventional LLDPE resins.

The linear polyethylene blend components of the invention may be prepared by use of catalyst systems of the metallocene type known to provide narrow CD/MWD resins. Cyclopentadienylide catalyst systems using a metallocene complex in conjunction with an alumoxane

cocatalyst or reaction product thereof are suitable for preparing the polymer components utilized in the blends of the invention. The metallocene catalyst may be represented by the general formula $(C_p)_mMR_nR'_p$ wherein C_p is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IVB, or VB transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M. Various forms of the catalyst system of the metallocene type may be used for polymerization to prepare the polymer components of the present invention including those of the homogenous or the heterogeneous, supported catalyst type wherein the catalyst and alumoxane cocatalyst are together supported or reacted together onto an inert support for polymerization by gas-phase, high pressure, slurry, or solution polymerization.

The cyclopentadienyls of the catalyst may be unsubstituted or substituted with hydrogen or hydrocarbyl radicals. The hydrocarbyl radicals may include alkyl, alkenyl, aryl, alkylaryl, arylalkyl, and like radicals containing from about 1-20 carbon atoms or where 2 carbon atoms of cyclopentadienyl are joined together to form a C_4-C_6 ring. Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like. Exemplary halogen substituents include chlorine, bromine, flourine and iodine. Of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the like. Illustrative, but non-limiting examples of the metallocene catalyst useful in preparing the polymers of the present invention include bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl,

bis(cyclopentadienyl)zirconium dimethyl,
bis(cyclopentadienyl)zirconium diphenyl,
bis(cyclopentadienyl)hafnium dimethyl and diphenyl,
bis(cyclopentadienyl)titanium di-neopentyl,
bis(cyclopentadienyl)zirconium di-neopentyl,
bis(cyclopentadienyl)titanium dibenzyl,
bis(cyclopentadienyl)zirconium dibenzyl,
bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)titanium methyl iodide, bis(cyclopentadienyl)titanium ethyl bromide, bis(cyclopentadienyl)titanium ethyl iodide, bis(cyclopentadienyl)titanium phenyl bromide, bis(cyclopentadienyl)titanium phenyl iodide, bis(cyclopentadienyl)zirconium methyl bromide, bis(cyclopentadienyl)zirconium methyl iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopentadienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium phenyl bromide, bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl metallocenes such as cyclopentadienyltitanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienylzirconium trimethyl, cyclopentadienylhafnium triphenyl, cyclopentadienylhafnium trineopentyl, and cyclopentadienylhafnium trimethyl.

Other metallocenes which may be usefully employed to prepare the polymer components of the invention include the monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride,

pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH_2 and derivatives of this reagent such as bis(cyclopentadienyl)$Ti=CH_2.Al(CH_3)_3$, $(Cp_2TiCH_2)_2$, $Cp_2TiCH_2CH(CH_3)CH_2$, $Cp_2Ti-CHCH_2CH_2$; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride and other dihalide complexes; silicon, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes and the like.

Additional zirconocene catalysts useful according to the present invention include bis(cyclopentadienyl) zirconium dimethyl; bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl) zirconium methylchloride, pentamethylcyclopentadienyl zirconium trichloride, pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethylcyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopentadienes, such as bis(ethylcyclopentadienyl)zirconium dimethyl, bis(β-phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, bis(n-butyl-cyclopentadienyl)zirconium dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl, bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)zirconium

di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl and dihalide complexes of the above; silicon, phosphorus, and carbon bridged cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl ethylene bridged bis(tetrahydroindenyl) zirconium dimethyl or dihalide, carbenes represented by the formula $Cp_2Zr=CHP(C_6H_5)_2CH_3$, and derivatives of these compounds such as $Cp_2\overline{ZrCH_2CH(CH_3)CH_2}$.

Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)vanadium dichloride and the like are illustrative of other metallocenes.

The alumoxanes are polymeric aluminum compounds which can be represented by the general formulae $(R\text{-}Al\text{-}O)_n$ which is a cyclic compound and $R(R\text{-}Al\text{-}O\text{-})_nAlR_2$, which is a linear compound. In the general formula R is a C_1-C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 2 to about 20. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained.

The alumoxane can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in the form of a moist solvent. In an alternative method, the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate.

Preferably, the alumoxane is prepared in the presence of a hydrated ferrous sulfate as described in U.S. Patent 4,665,208. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with ferrous sulfate represented by the general formula

$FeSO_4.7H_2O$. The ratio of ferrous sulfate to aluminum trimethyl is desirably about 1 mole of ferrous sulfate for 6 to 7 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The ratio of aluminum in the alumoxane to total metal in the metallocenes can be in the range of about 0.5:1 to about 10,000:1, and preferably about 5:1 to about 1000:1.

Various inorganic oxide supports may be used for supported catalyst systems to prepare interpolymers and blend components of the present invention. The polymerization is generally carried out in the temperature range of about 0-160°C, or even higher, but this range is not meant to be exclusive for preparing the interpolymer and blend components of the invention, which may be prepared by any technique resulting in the structure set forth. Atmospheric, sub-atmospheric, or super-atmospheric pressure conditions have been used for the polymerization using the metallocene catalyst described above. It is generally preferred to use catalyst compositions at a concentration so as to provide from about 1 ppm to about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of transition metal based on the weight of monomers in the polymerization of the ethylene polymers.

A slurry polymerization process generally uses super-atmospheric pressures and temperatures in the range of 40-110°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

In a modification, the polymer components of the present invention may be formed by gas-phase

polymerization. A gas-phase process utilizes super-atmospheric pressure and temperatures in the range of about 50°-120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperature of 50°-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other adventitious impurities. Polymer product can be withdrawn continuously or semi-continuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal. The polymer obtained can be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives may be added to the polymer, as is known in the art.

The blends of the present invention are prepared by blending the desired components in the desired proportions using conventional blending, techniques and apparatus, such as, for example, screw-type extruders, Banbury mixers, and the like. Alternatively, the blends may be made by direct polymerization, without isolation of the blend components, using, for example, two or more catalysts in one reactor, or by using a single catalyst and two or more reactors in series or parallel. The blend may also be compounded with various conventional additives known in the art such as, for example, antioxidants, UV stabilizers, pigments, fillers, slip additives, block additives, and the like. The blend preferably does not

contain any blend components in proportions which would significantly adversely affect any improved properties desired to be obtained by blending the LLDPE resins.

The invention is illustrated by way of the following examples:

Example 1

An ethylene homopolymer resin, identified as '006, having characteristics shown in Table 1, was prepared in a gas phase reactor employing a silica supported transition metal catalyst described below.

The gas phase reaction was carried out at 185°F reaction temperature, 195 psi ethylene pressure, a hydrogen/ethylene mole ratio of 0.00041, and a residence time of 2 hours. A second polymer, an ethylene/butene-1 copolymer identified as '013, having characteristics shown in Table 1 was prepared in the gas phase reactor using the same supported catalyst as described below. The gas phase reaction was carried out at 140°F reactor temperature, 195 psi ethylene pressure, a hydrogen/ethylene mole ratio of 0.00061, a butene-1/ethylene mole ratio of 0.123, and a residence time of 2 hours.

The silica supported transition metal catalyst was obtained as follows:

100 grams of high surface area (Davison 952) silica, dehydrated in a flow of dry nitrogen at 800°C for 5 hours, was slurried with 500 cc of toluene at 25°C under nitrogen in a 2500 cc round-bottom flask using a magnetic stirrer. 250 cc of methyl alumoxane in toluene (1.03 mole/liter in aluminum) was added dropwise over 15 minutes with constant stirring to the silica slurry. Stirring was continued for 30 minutes while maintaining the temperature at 25°C. To the alumoxane treated silica slurry was added dropwise over 15 minutes, with constant stirring 250.0 cc of toluene solution containing 2.00 grams of bis(n-butylcyclopentadienyl)zirconium dichloride. This slurry was stirred an additional one half hour while maintaining the temperature at 65°C and thereafter the

toluene was decanted and the solids recovered and dried in vacuo for 4 hours. Analysis of the catalyst indicated that it contained 4.5 wt% aluminum and 0.63 wt% zirconium.

Resins '006 and '013 were then intensively mixed at 360°F in equal proportions in a Banbury melt blender along with 1000 ppm each of the stabilizers Irganox 1076 and Irgafos 168. The molten blend from the Banbury was transferred to a roll mill, made into a thin sheet and then cooled to room temperature. The cold sheet was then chopped into approximately 1/8 inch chips. Characteristics of this blend, identified as Blend B1, are given in Table 1.

Compression molded sheets, five thousandth of an inch in thickness, were prepared by melting the chopped blend at 160°C in a press, compressing to 20 tons pressure for 5 minutes and then cooling the blend under pressure to room temperature at a rate of 15°C per minute. Properties of the molded sheet specimen are shown in Table 2.

Example 2

A second compression molded sheet was prepared and tested as in Example 1, from the resins described in Example 1, except that the blend which is identified as Blend B2, consisted of one part '006 and three parts '013. Characteristics of Blend B2 are given in Table 1, properties of Blend B2 are given in Table 2.

TABLE 1
POLYMER CHARACTERIZATION

Sample Designation	Mole% Butene[a]	Mw[b]	Mw/Mn[b]	Density[c]	Melt Index[d]	CDBI[e]
'006	0.0%	76,700	2.8	0.9552	5.0	100%
'013	6.4	80,400	2.3	0.9042	4.0	67%
Blend B1	2.7	76,500	2.4	0.9335	4.4	25%
Blend B2	4.9	76,900	2.3	0.9172	4.3	44%

a. By C-13 NMR
b. Weight average molecular weight (Mw), and ratio of number average molecular weight (Mn), Mw/Mn by size exclusion chromatography.

c. Density by gradient column method, ASTM D1585, g/cm^3
d. Melt index by ASTM D1738 Condition E, dg/min
e. CDBI, composition distribution breadth index, is defined as the weight percent of polymer molecules having a comonomer content within 50% of the median total molar comonomer content CDBI; of HDPE is defined to be 100%. Determined using temperature rising elution fractionation using tetra-chloroethylene solvent over a 6°C to 120°C temperature range as described in U.S. Patent Application Serial Number 151,350. See also Wild, et al, J. Poly. Sci. Ed, Vol. 20, p 441 (1982).

TABLE 2
TEAR AND TENSILE STRENGTH OF MOLDED SHEET

Sample Designation	Tear Strength[e]	Tensile Strength[f] @ Yield	Tensile Strength[f] @ Break	Elongation[f] @ Yield	Elongation[f] @ Break	Modulus[f] Secant	Modulus[f] Tangent
'006	48	3640 psi	840	18%	710%	127,000	155,000
'013	111	800	3230	70	1830	165,000	---
Blend B1	210	1900	2870	23	1620	70,600	76,000
Blend B2	227	1330	3030	28	1530	37,700	42,000

e. Tear strength, in g/mil, measured using ASTM 1922, tear resistance by pendulum method
f. Tensile strength, elongation, and modulus measured using ASTM D638

Example 3

Polymers used as blend components were synthesized by a procedure similar to that described below for Run 03. A stainless steel, 1-liter Zipperclave autoclave reactor was used in the syntheses. The reactor was equipped with a water jacket for heating and cooling, a septum inlet for injection of liquid components, a burette for measuring and adding purified hexane, and a controlled pressure source of purified ethylene and nitrogen. Polymerization reactions were started by cleaning the reactor and purging it with purified nitrogen for several hours. 800 cc of purified hexane was added to the reactor vessel at 25°C by means of the measuring burette.. 100 cc of purified 1-hexene was then added under nitrogen, and the contents of the reactor were continuously stirred at 1200rpm henceforth. 10.0 cc of the 10 wt% solution of methylalumnoxane was added by syringe, and the reactor temperature was equilibrated at the reaction temperature of 60°C. Hydrogen was not used in this example

it is added at this time in the examples which do use it. Hydrogen was metered into the reactor from a vessel of known volume equipped with a highly precise pressure gauge. The ideal gas law was used to calculate the millimoles of hydrogen introduced into the reactor. 1.00 cc of a solution of 0.01 wt% bis(n-butylcyclopentadienyl) zirconium dichloride in distilled toluene was then injected by syringe, followed by pressurization immediately with 90.9 psi of purified ethylene. Ethylene was fed continuously on demand to the stirring reactor while maintaining the reaction temperature at 60°C and the reaction pressure at 90 psi. After 10 minutes of polymerization the reaction was stopped by rapidly cooling and venting the pressure and exposing the contents to air. The polymer was obtained by evaporating the liquid components and drying in a vacuum oven for 1 hour. The poly(ethylene-co-hexene-1) polymer obtained, which is identified as CO3, was obtained in 89.7 yield.

Other polymerizations runs were performed using the procedure above with the exception that the volumes, temperatures, and other polymerization conditions were modified as shown in Table 3. Characterization data for the blend components are given in Table 4.

Blends 8A, 9D, 20C, 21F and 22E were each prepared using equal quantities of three blend components. (The letter designation in these blends corresponds to the type of blend illustrated in Figure 1.) Blend components for each of the blends are given in Table 4, and they were blended by the following solution blending procedure using ca. 14 g. of each blend component. 2000 cc of xylene was purged with nitrogen for one hour, the three blend components were added, and the mixture was stirred and heated to 144°C to dissolve the polymers. The polymer solution was then cooled to 70°C, and 2000 cc of methanol was added to precipitate the polymer. The mixture was then cooled to 22°C, and the precipitated polymer was

filtered and dried in a vacuum oven. Average composition, composition distribution breadth index, molecular weight data, and density of the blends are listed in Table 4.

Compression molded sheets, five thousandth of an inch in thickness, were prepared by melting the blended polymers in a press, compressing to 20 tons pressure for 5 minutes and then cooling the blend under pressure to room temperature. Properties of the molded sheet specimen are shown in Table 5 for blends 8A, 9D, 20C, 21F and 22E. The fraction of polymer extracted by hexane at 69°C is also given for the blends.

Table 5 shows that the tear strength of blends 9D, 20C, 21F and 22E, i.e., blends having novel composition-molecular weight distributions, are each superior to that of blend 8A, which has a conventional-type composition-molecular weight distribution. In many applications it is desirable to have low levels of extractable polymer, and the table shows that blends 9D, 20C, 21F, and 22E are markedly superior to blend 8A in this respect. Moreover, tensile properties such as tensile strength at yield of the conventional-type blend 8A are generally comparable to the tensile strengths of the other blends. Consequently, the benefits of high tear strength and low levels of extractables can be achieved without undue loss of tensile properties.

This example illustrates the benefits obtained by certain novel composition-molecular weight distributions differing from the conventional type. Thus, blends 9D and 20C have similar average molecular weights and molecular weight distributions. Consequently, flow and melt fabrication performance of these blends should be similar to that of the conventional-type blend 8A. Therefore, the desirable mechanical and solubility properties of blends 9D and 20C are not obtained at the expense of fabrication performance. Additionally, blends 21F and 22E have much lower weight average molecular weight than blend 8A, and

they should therefore be more easily fabricated into articles of commerce such as films, fibers and molded objects.

In summary, in the blends of this example (Type C, D, E and F blends) the average molecular weight and molecular weight distribution can be manipulated independently of the composition distribution. Superior solid state performance can therefore be achieved without sacrificing melt fabrication performance.

TABLE 3
POLYMERIZATION CONDITIONS

Polymerization Run No.	Reaction Temp.°C	$C_2^=$ Press. (psi)	Time (min.)	Hexane (cc)	1-Hexene (cc)	Catalyst Solu. (cc)	Yield gm	H_2 m mole
03	60	90	10	800	100	1.0	89.7	--
09	80	60	10	800	75	1.0	36.6	--
15	80	60	15	800	--	1.0	47.0	10
19	80	60	60	800	75	0.25	44.2	5
27	90	60	45	800	150	0.50	96.5	--
30	75	75	42	800	87.5	0.55	86.3	--
38	60	130	20	800	150	0.20	89.5	--
42	60	60	30	800	--	1.0	81.0	--
48	70	170	9	300	600	0.5	114.0	--
64	68	302	60	--	800	0.05	53.0	--

TABLE 4
POLYMER CHARACTERIZATION OF BLENDS AND BLEND COMPONENTS

Sample Designation[h]	Mole % Hexene[a]	Mw[b]	Mw/Mn[b]	Density[b]	CDBI[b]
C27	6.1	12,500	1.9	--	77%
C30	2.0	48,800	1.9	--	81
C42	0.0	259,000	2.0	--	100
Blend 8A[c]	2.7	113,000	9.0	0.933	24
C15	0.0	13,400	2.7	--	100
C30	2.0	48,000	1.9	--	81
C64	4.2	223,000	2.2	--	--
Blend 9D[d]	2.1	95,600	9.8	0.940	42
C19	2.3	13,600	1.9	--	70
C30	2.0	48,800	1.9	--	81
C38	2.2	240,000	2.2	--	--
Blend 20C[e]	2.3	94,800	8.8	0.932	64
C15	0.0	13,400	2.7	--	100
C09	3.0	52,000	2.4	--	79
C03	3.1	121,000	2.2	--	67
Blend 21F[f]	--	62,000	6.4	0.946	46
C15	0.0	13,400	2.7	--	100
C09	3.0	52,000	2.4	--	79
C48	7.2	50,000	1.9	--	75
Blend 22E[g]	--	37,800	4.2	0.940	37

(a) Calculated from absorbance of 1378 cm^{-1} IR band using spectral substraction to correct for overlap of adjacent IR bands. Residual peak at 1378 cm^{-1} was converted to hexene content using calibration obtained by C13 NMR analysis of poly(ethylene-co-hexenes).

(b) Same as in Table 1

(c) Blend 8A consisted of equal quantities of C27, C30 and C42

(d) Blend 9D consisted of equal quantities of C15, C30 and C64

(e) Blend 20C consisted of equal quantities of C19, C30 and C38

(f) Blend 21F consisted of equal quantities of C15, C09 and C03

(g) Blend 22E consisted of equal quantities of C15, C09 and C48

(h) Blend components in this table are identified by the letter C followed by the corresponding polymerization run number from Table 3. For example, blend component C27 was obtained from polymerization run 27.

TABLE 5
PROPERTIES OF MOLDED SHEET

Sample	Tear Strength g/mil	Tensile Strength at Yield, psi	Hexane Extractable Polymer %
Blend 8A	68	1770	22
Blend 9D	241	1980	3.0
Blend 20C	426	1400	6.3
Blend 21F	205	2050	4.5
Blend 22E	107	2050	6.7

(a) Tear strength measured by ASTM 1922, tear resistance by pendulum method.
(b) Tensile strength at yield measured using ASTM D638.
(c) Extractables were determined as follows. About 0.5 g of polymer molded sheet, ca. 5 mil thick, was weighed and placed in a weighed cellulose extraction thimble. The thimble and polymer were placed in a vapor jacketed Soxlet-type extractor, and the polymer was extracted with condensed vapors of boiling hexane at 69°C for 16 hours. The thimble and residual polymer were removed, dried in a vacuum oven, and weighed to determine the amount of extracted, i.e., soluble, polymer.

The foregoing description of the invention is illustrative and explanatory thereof. Various changes in the materials, apparatus, and particular steps employed will occur to those skilled in the art. It is intended that all such variations within the scope and spirit of the appended claims be embraced thereby.