EXHIBIT V

PART 10

Claims:

1. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

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

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

c) a critical shear stress at onset of gross melt fracture greater than 4×10^6 dyne/cm^2.

2. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

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

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

c) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

3. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63, and

b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5.

4. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

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

b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5, and

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n.

5. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n.

6. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

(a) from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone and

(b) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 dynes/cm^2.

7. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

(a) from about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone and

(b) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n.

8. An olefin polymer characterized in that the olefin polymer is a substantially linear olefin polymer having:

(a) from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone,

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

(c) a molecular weight distribution, M_w/M_n from 1.5 to 2.5.

9. The substantially linear olefin polymer of any of claims 1-8,

wherein the substantially linear olefin polymer is:

(A) a homopolymer of a C_2-C_{20} olefin, or

(B) an interpolymer of ethylene with at least one C_2-C_{20} acetylenically unsaturated monomer, or

(C) an interpolymer of ethylene with at least one C_4-C_{18} diolefin.

10. The substantially linear olefin polymer of any of claims 1-8,

wherein the substantially linear olefin polymer is:

(A) an ethylene homopolymer, or

(B) an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

11. The substantially linear olefin polymer of any of Claims 1-7 wherein the substantially linear olefin polymer has a M_w/M_n less than 3.5.

12. The substantially linear olefin polymer of any of Claims 1-7 wherein the substantially linear olefin polymer has a M_w/M_n from 1.5 to 2.5.

13. The substantially linear olefin polymer of any of Claims 1-5 wherein the substantially linear olefin polymer has from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone.

14. A process of preparing a substantially linear ethylene polymer having a melt flow ratio, $I_{10}/I_2 \geq 5.63$, and a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, said process characterized by continuously contacting one or more C_2-C_{20} olefins with a catalyst composition under polymerization conditions, wherein said catalyst composition is characterized as:

a) a metal coordination complex comprising a metal atom of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π–bonded moiety substituted with a constrain inducing moiety,

said complex having a constrained geometry about the metal atom such that the angle at the metal atom between the centroid of the delocalized, substituted π-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π-bonded moiety lacking in such constrain-inducing substituent,

and provided further that for such complexes comprising more than one delocalized, substituted n-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π-bonded moiety, and

b) an activating cocatalyst.

15. The process of Claim 14 wherein the process is:

(A) a gas phase process, or

(B) a suspension process, or

(C) a solution process, or

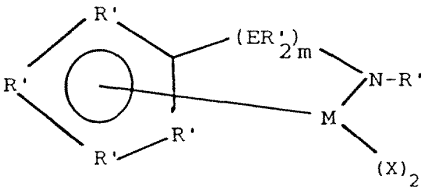
(D) a slurry process.

16. The solution process of Claim 15 wherein the polymerization conditions comprise a reaction temperature and olefin concentration sufficient to form the substantially linear olefin polymer.

17. The process of Claim 16 wherein the polymerization conditions comprise a reaction temperature and olefin concentration sufficient to form a substantially linear olefin polymer having a I_{10}/I_2 of at least 8.

18. The process of Claim 16 wherein the polymerization conditions comprise a reaction temperature and an olefin concentration sufficient to form the substantially linear olefin polymer, wherein the polymer has a I_{10}/I_2 of at least 9.

19. The process of Claim 14 wherein (a) is an amidosilane- or amidoalkanediyl- compound corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound to an η^5-cyclopentadienyl group;

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, alkyl, or aryl of up to 20 carbons; and

m is 1 or 2.

20. The process of Claim 14 wherein (b) is:

(A) methylaluminoxane or

(B) tris(pentafluorophenyl)borane.

21. The product obtainable by the process of Claim 14.

22. A composition comprising an olefin polymer and at least one other natural or synthetic polymer, wherein the olefin

polymer is characterized as the substantially linear olefin polymer of any of Claims 1-8.

23. A composition comprising an olefin polymer and at least one other natural or synthetic polymer, wherein the olefin polymer is characterized as:

(A) an ethylene/α–olefin substantially linear olefin polymer, or

(B) a substantially linear ethylene homopolymer.

24. The composition of Claim 23 wherein the synthetic polymer is a conventional Ziegler polymerized ethylene/α–olefin polymer.

25. A fabricated article comprising an olefin polymer, characterized in that the olefin polymer is the substantially linear olefin polymer of any of Claims 1-8.

26. The fabricated article of Claim 25 wherein the article is:

(A) a film, or

(B) a fiber, or

(C) a sheet, or

(D) a woven fabric, or

(E) a nonwoven fabric, or

(F) a molded article, or

(G) a wire and cable coating.

27. The fabricated article of Claim 25 wherein the film is a blown film.

28. The blown film of Claim 27 wherein the substantially linear olefin polymer is an ethylene/α-olefin copolymer having a density from 0.9 g/cm^3 to 0.92 g/cm^3.

29. The blown film of Claim 28 wherein the ethylene/α-olefin copolymer has a molecular weight distribution, M_W/M_n, from 1.5 to 2.5.

30. The blown film of Claim 29 wherein the film has a heat seal strength equal to or higher than a film made from a heterogeneous Ziegler polymerized polymer at the same heat seal temperature, wherein the substantially linear ethylene polymer and the heterogeneous Ziegler polymerized polymer have about the same melt index and about the same density.

WO 93/08221 PCT/US92/08812

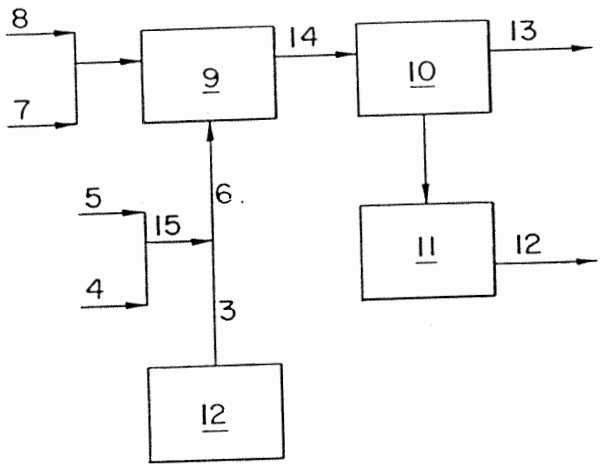


FIG. 1

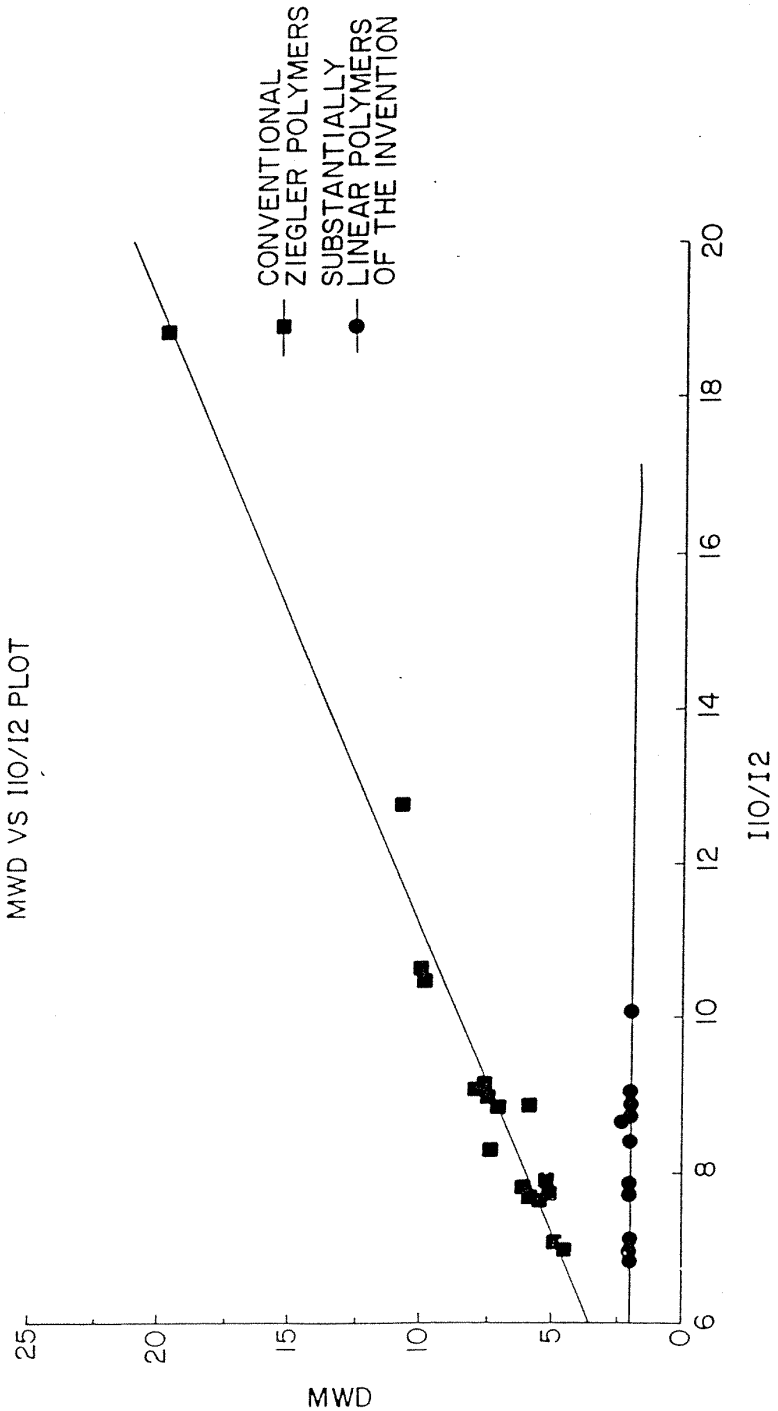


FIG. 2

SUBSTITUTE SHEET

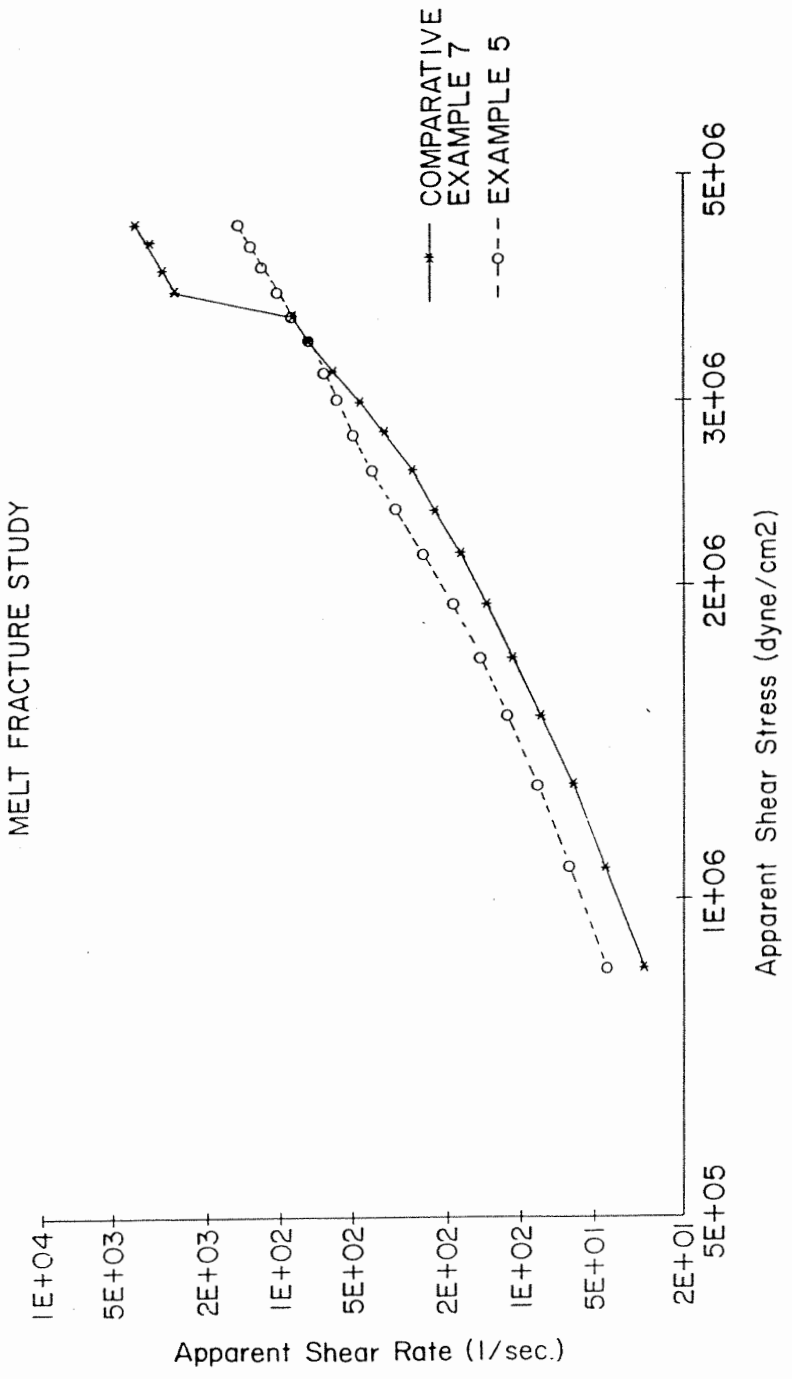

MELT FRACTURE STUDY
COMPARATIVE EXAMPLE 7
EXAMPLE 5
Apparent Shear Stress (dyne/cm2)
5E+05
1E+06
2E+06
3E+06
5E+06
Apparent Shear Rate (1/sec.)
2E+01
5E+01
1E+02
2E+02
5E+02
1E+02
2E+03
5E+03
1E+04

FIG.3

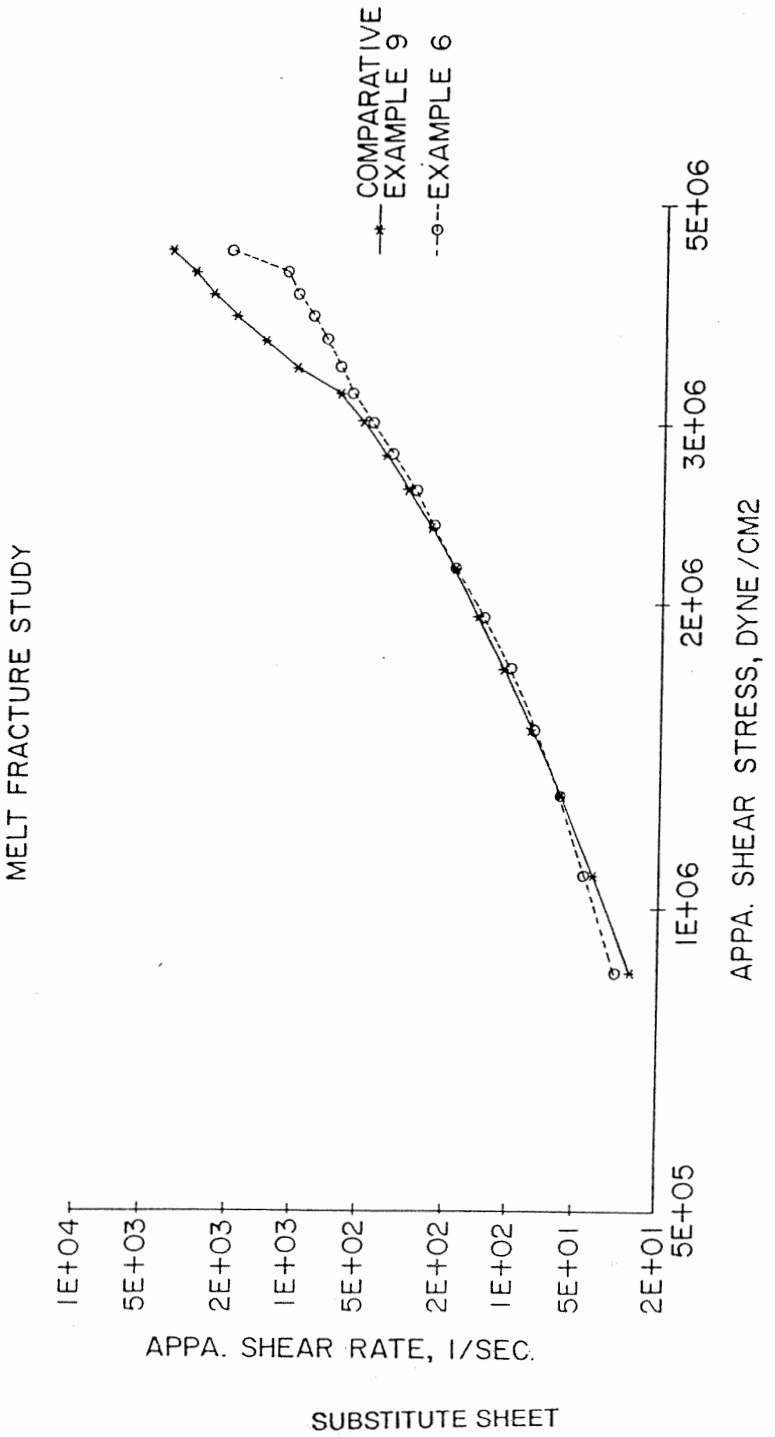

MELT FRACTURE STUDY
COMPARATIVE EXAMPLE 9
EXAMPLE 6
APPA. SHEAR STRESS, DYNE/CM2
5E+06
3E+06
2E+06
1E+06
5E+05
APPA. SHEAR RATE, 1/SEC.
1E+04
5E+03
2E+03
1E+03
5E+02
2E+02
1E+02
5E+01
2E+01

FIG.4

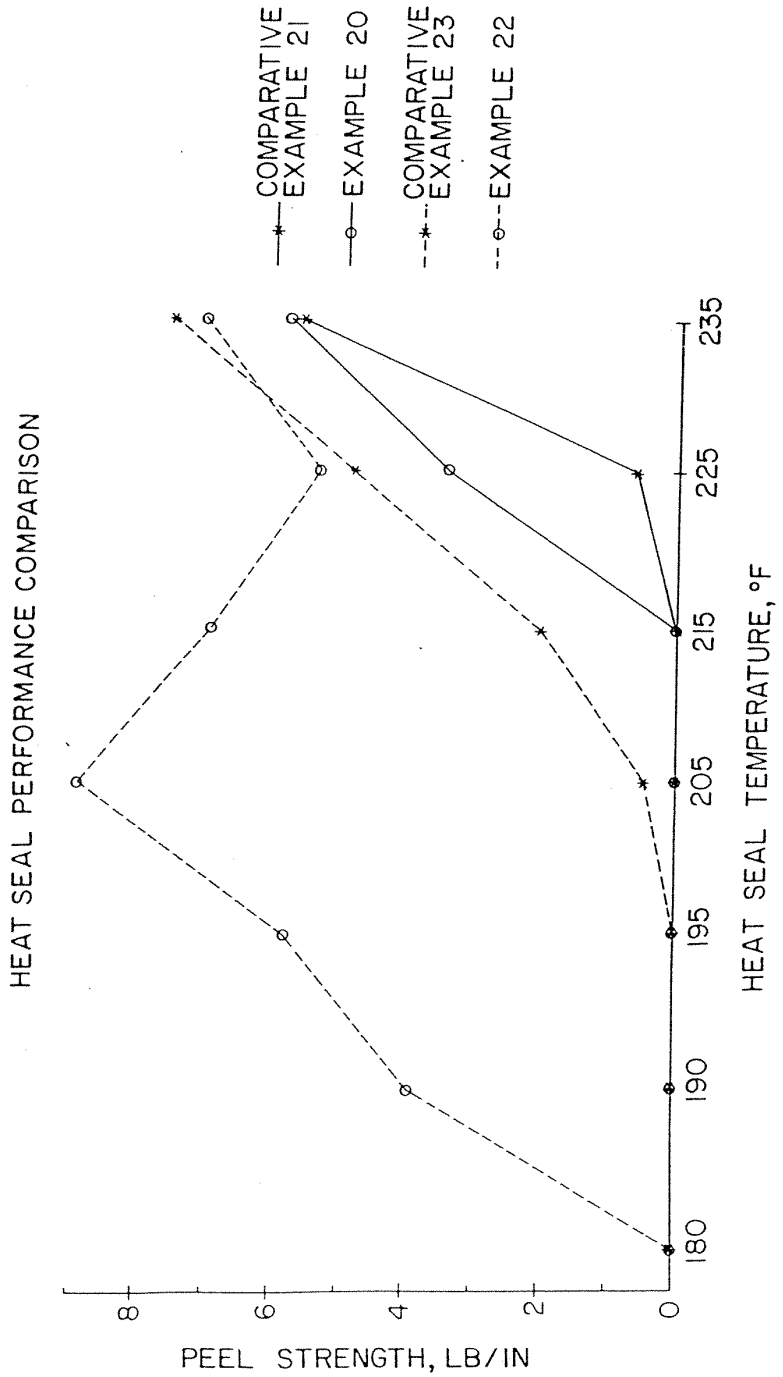

COMPARATIVE EXAMPLE 21
EXAMPLE 20
COMPARATIVE EXAMPLE 23
EXAMPLE 22
HEAT SEAL PERFORMANCE COMPARISON
PEEL STRENGTH, LB/IN
0
2
4
6
8
HEAT SEAL TEMPERATURE, °F
180
190
195
205
215
225
235

FIG.5

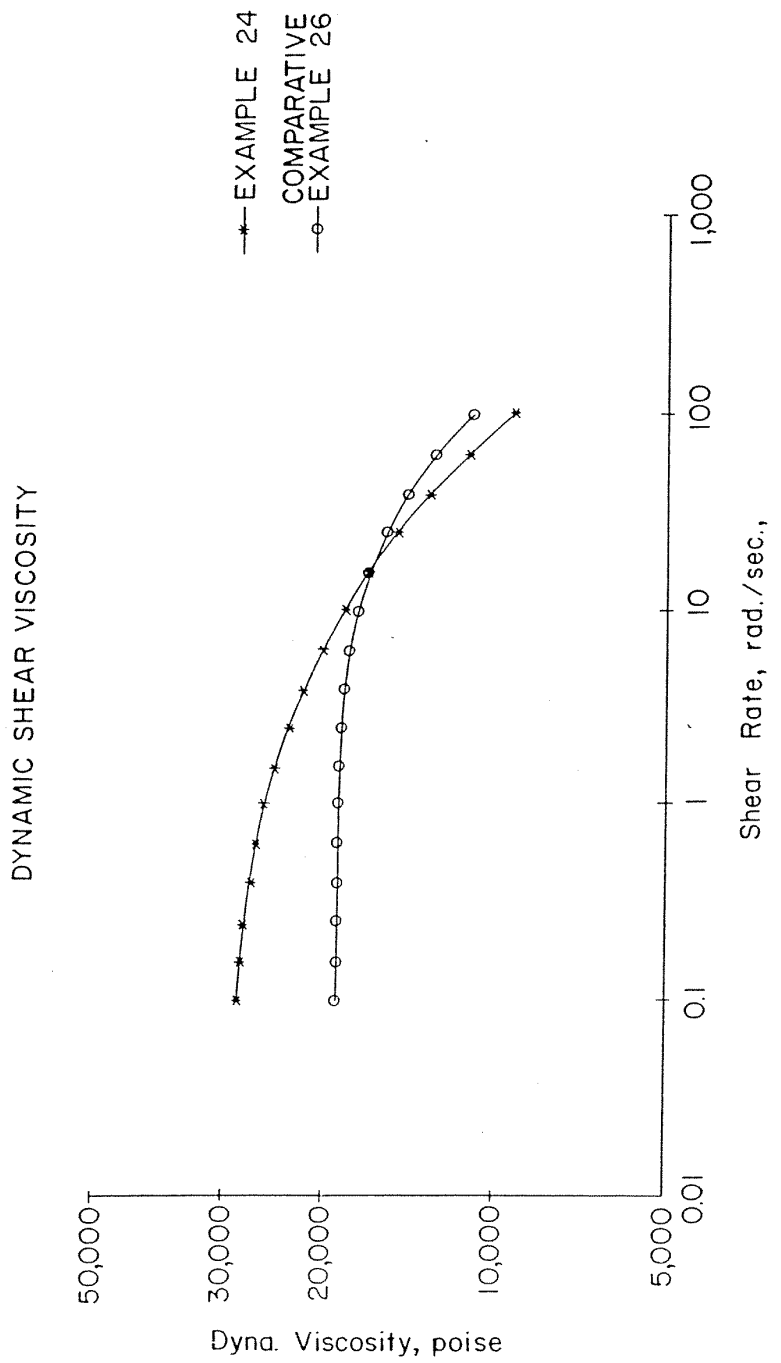

EXAMPLE 24
COMPARATIVE EXAMPLE 26
DYNAMIC SHEAR VISCOSITY
Shear Rate, rad./sec.,
0.01
0.1
1
10
100
1,000
5,000
10,000
20,000
30,000
50,000
Dyna. Viscosity, poise

FIG.6

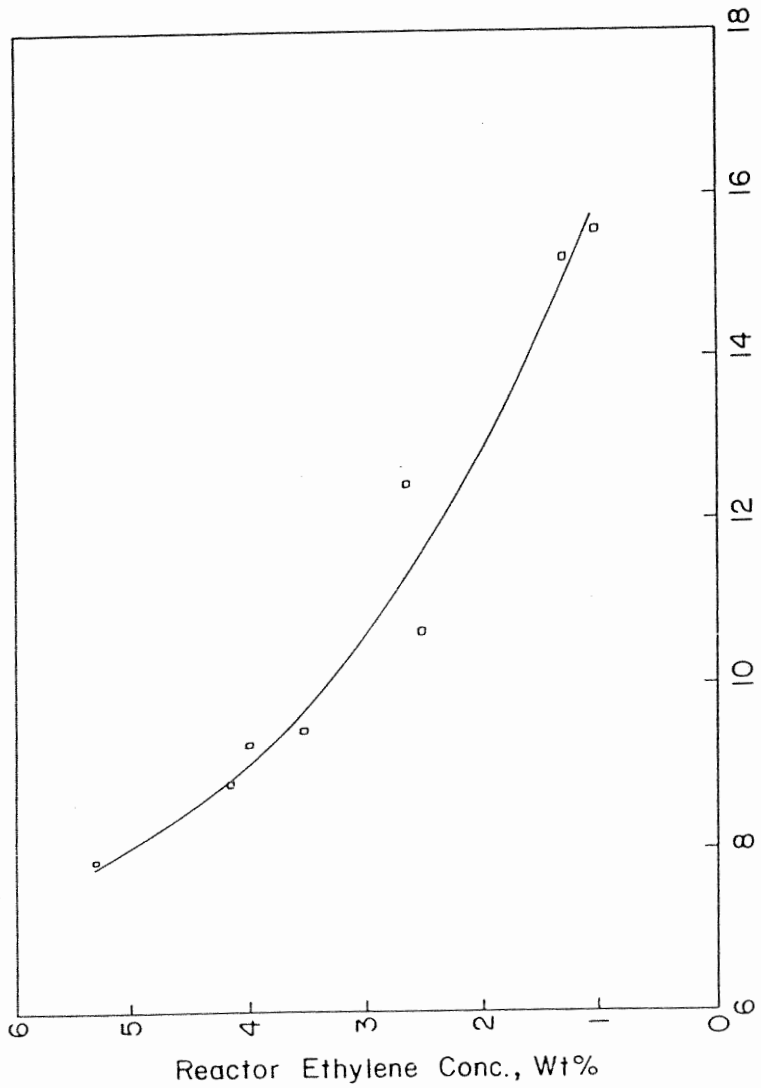

Product I10/I2
Reactor Ethylene Conc., Wt%
0
2
4
6
8
10
12
14
16
18
1
3
5

FIG. 7

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08L 23/04, C08J 5/18 — A1

(11) International Publication Number: WO 94/06857

(43) International Publication Date: 31 March 1994 (31.03.94)

(21) International Application Number: PCT/US93/08586

(22) International Filing Date: 13 September 1993 (13.09.93)

(30) Priority data:
07/945,759 16 September 1992 (16.09.92) US

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(81) Designated States: BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: SOFT FILMS HAVING ENHANCED PHYSICAL PROPERTIES

(57) Abstract

The present invention provides for a polymer composition comprising a blend of from 25 to 90 % by weight of a very low density ethylene polymer having a density on the range of from 0.88 to 0.925 g/cm^3, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution not greater than 3.5 and a compositional distribution breadth index greater than 70 %, and from 10 to 75 % by weight of a low to medium density ethylene polymer having a density of from 0.910 to 0.935, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution greater than 3.5 and a compositional breadth index less than 70 %. The invention also provides for films prepared from this blend having single layer construction or having laminar ABA construction wherein the A or skin layers comprise the blend of this invention and the B or core layer comprises a different olefin polymer such as high density polyethylene. Films of this invention exhibit excellent elongation, tensile and impact properties and also softness, feel and noise properties which render them eminently suitable for use as back sheet components in the fabrication of absorbent articles such as diapers, bed pads and like articles where such properties are desirable.

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SOFT FILMS HAVING ENHANCED PHYSICAL PROPERTIES

FIELD OF THE INVENTION

The present invention relates to polymer compositions and soft, tough film materials prepared therefrom which are useful in the fabrication of personal hygiene products such as diapers, bed pads and the like.

BACKGROUND OF THE INVENTION

The many applications for polyolefin film materials include their use as back sheet materials in the construction of diapers, bed pads and similar articles. Such articles are normally constructed of an absorbent inner layer disposed between a non-woven top sheet and a back sheet film. Films based on olefin polymers such as low density polyethylene, linear low density polyethylene, polypropylene and copolymers of ethylene with one or more comonomers such as vinyl acetate, acrylic acid, acrylic acid esters and other olefin monomers containing from 3 to 8 carbon atoms have been particularly preferred for such uses. These materials can be formulated to possess the requisite properties of flexibility and moisture impermeability which render them suitable for such applications.

It is also desirable that film materials used in such applications meet other criteria. For example, because such films come into contact with the user, they should be soft to the touch similar to cloth materials, and also, be quiet when rumpled or crinkled. They should at the same time also possess good physical properties such as tensile, elongation,puncture strength and impact strength so that they are not readily torn or punctured under conditions of normal or more rugged use.

One of the more preferred polymer materials which has been used in the preparation of the aforementioned film materials is linear low density polyethylene (LLDPE), mainly because of its film strength and toughness. LLDPE may be produced by copolymerizing ethylene with a C_4 to C_{10} alpha-olefin. Generally the preferred alpha-olefins include those selected from butene-1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1, and octene-1 The comonomers are present in amounts up to 20 weight percent, normally, between 3 and 14 weight percent(wt. %). The polymerization is conducted at low pressure using a chromium catalyst or Ziegler catalyst and may be carried out in the gas phase. The LLDPE produced by such methods has a density between 0.900 and 0.935 g/cm3 and a melt index (MI) between 0.1 and 25.0 grams/10 min, more preferably from 0.1 to 5.0 grams /10 min. Manufacturing processes for the production of LLDPE are known such as

disclosed in U.S. Patents 4,076,698 and 4,205,021.

Despite the good properties of films made using LLDPE, the melt processing properties of the polymer tend to restrict the process conditions under which cast films having a uniform thickness can be made. For example, a typical process for preparing an embossed film for use as diaper backsheet material is the slot-die cast extrusion process wherein the polymer is heated to a temperature generally in the profile range of about 175°C to about 290°C (350°F to 550°F) in an extruder and extruded through a slot die into the nip of a steel and rubber roll system. Where the film is to be embossed, the steel roll is engraved with a pattern of either protrusions (a male embossing roll) or depressions (a female embossing roll). The rubber roll serves as a backing roll into which the steel roll pattern is impressed during the formation of the film. Thus the roll system serves both to film-form and texture the polyolefin material. The speed of the rubber and steel rolls is maintained to permit continuous embossing of the film and subsequent take up of the film on a wind up roller after it exits the steel/rubber roller nip.

In terms of process efficiency, the film manufacturer is highly motivated to adjust processing conditions such as temperature, roll speeds and take-up speeds to maximize the rate of film production on the one hand while on the other hand producing a quality film having a substantially uniform film thickness, which is generally in the range of about 19 μ to about 51 μ (0.75 to 2 mils).

A particular property of LLDPE which tends to restrict the line speed at which film made from this polymer can be processed is caused by a phenomena referred to as draw resonance. Draw resonance is defined as the inability of the film to hold a constant film thickness down the film web in the machine or take-up direction, which is evidenced by the presence of light and dark bands running across the film. The light areas are a thinner gauge and the darker areas are of a thicker gauge. The degree of draw resonance is a direct function of line speed, becoming worse at higher line speeds. As a result, the maximum line speed at which good quality film can be produced is restricted by the onset of draw resonance.

Attempts have been made to improve the draw resonance of LLDPE by utilizing a blend of this material with up to 50% by weight of another polyethylene having a higher Melt Index than LLDPE, such as high pressure low density polyethylene (LDPE) having a Melt Index of at least 7.5 dg/min and a density in the range of from 0.910 to 0.930 g/cm^3 or as an alternative EVA's can be blended with LLDPE. However, draw resonance is still found to occur at higher line speeds

(e.g., 254 cm/sec (500 fl/min)) with such blends and the presence of a substantial amount of the LDPE in the blend serves to diminish the good tensile and elongation properties of film material when compared with material containing LLDPE as the sole polymer.

Recently, a new class of low density ethylene polymers have been introduced into the marketplace. These materials are characterized as very low density ethylene polymers having a density in the range of from .0.88 to 0.915 g/cm3, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution (MWD) of no greater than 3.5 and a compositional distribution breadth index (CDBI) greater than 70 percent. Compositionally, these polymers contain ethylene copolymerized with up to 15 mole % of another alpha monoolefin containing from 3 to 20 carbon atoms such as butene-1, hexene-1, octene-1 and the like. These polymers with narrow MWD and narrow CD provide a unique balance of properties including narrow melting point range and improved toughness when fabricated into shaped articles as compared with normal low density polyethylene prepared by the conventional Ziegler catalyst systems.

One of the primary uses of such materials is as a heat seal component as is shown in PCT Publication No. WO/93/03093 or layer used in conjunction with the preparation of packaging films constructed from polyolefin polymers such as polypropylene as is shown in PCT Publication No. WO/92/14784. The narrow melting point range of these polymers renders them extremely useful in packing fill operations where it is desirable to develop strong seal strength immediately after packaging and while the film is still hot from the sealing operation.

SUMMARY OF THE INVENTION

The present invention provides for a polymer composition comprising a blend of from 25 to 90% by weight of a very low density ethylene polymer having a density on the range of from 0.88 to 0.925 g/cm^3, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution not greater than 3.5 and a compositional distribution breadth index greater than 70%, and from 10 to 75% by weight of a low to medium density ethylene polymer having a density of from .910 to .935 g./cm3, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution greater than 3.5 and a compositional breadth index less than 70%.

The polymer composition of this invention may be fabricated into film material by cast extrusion processes and exhibit improved draw resonance such that film of uniform and constant thickness may be obtained at higher manufacturing take-up speeds.

The invention also provides for films prepared from this blend having single layer construction or having laminar ABA construction wherein the A or skin layers comprise the blend of this invention and the B or core layer comprises a different olefin polymer such as high density polyethylene.

Films of this invention exhibit excellent elongation, tensile and impact properties and also softness, feel and noise properties which render them eminently suitable for use as back sheet components in the fabrication of absorbent articles such as diapers, bed pads and like articles where such properties are desirable.

DETAILED DESCRIPTION OF THE INVENTION

The very low density ethylene polymers (VLDPE) which may be used as one component in the films of this invention are ethylene/alpha-monoolefin copolymers wherein the monoolefin can have from 4-20 carbon atoms such as ethylene/butene-1, ethylene/hexene-1 and ethylene/octene-1, copolymers or terpolymers of olefins having from 4-20 carbon atoms such as ethylene/butene-1/hexene-1. These ethylene copolymers and terpolymers with prescribed range of monomer levels can be prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene catalysts systems. The preferred range of comonomer level generally ranges from 4 to 15 mole percent.

These copolymers have a density in the range of 0.88 g/cm3 to 0.925 g/cm^3. Preferably the density is in the range of 0.885 g/cm^3 to 0.91 g/cm^3. Densities above 0.90 g/cm^3 are measured using standard accepted procedures. At densities below 0.90 g/cm^3, the samples are additionally conditioned by holding them for 48 hours at ambient temperature (23°C), prior to density measurement. Preferred copolymers in accordance with the present invention are VLDPE copolymers of ethylene and a C_4 to C_{10} alpha monoolefin, most preferably copolymers and terpolymers of ethylene and butene-1 and/or hexene-1.

The melt index (MI) of the ethylene/alpha-mono-olefin copolymers of the present invention is in the range of 0.5 dg/min to 7.5 dg/min. Preferably the MI is in the range of 0.5 dg/min to 5.0 dg/min, and the most preferred MI is in the range of 1.0 to 2.5 dg/min. MI as measured herein is determined according to ASTM D-1238 (190/2.16). High load MI is determined according to ASTM D-1238 (190/21.6). These copolymers also have a narrow molecular weight distribution. The ratio of Mw/Mn is generally in the range of 1.5 to 3.5, preferably in the range of 2.0 to 3.0.

The ethylene/alpha-mono-olefin copolymers should also have an essentially single melting point characteristic with a peak melting point (Tm) as determined by

Differential Scanning Colorimetry (DSC) in the range of 60°C to 115°C. Preferably the DSC peak Tm is in the range of 80°C to 100°C. "Essentially single melting point" as used herein means that at least 80% by weight of the material corresponds to a single Tm peak existing in the range of 60-115°C, and there is essentially absent from the polymer any substantial fraction of material which corresponds to a Tm peak found at a temperature higher than 115°C, i.e., "essentially" the bulk material content of the polymer corresponds to a "single" melting point peak in the 60-115°C range, and "essentially" no substantial fraction of the material has a peak melting point in excess of 115°C, as determine by DSC analysis.

DSC measurements are made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data i.e. the sample in heated at a programmed rate of 10°C/min to a temperature above its melting range. The sample is then cooled at a programmed rate of 10°C/min to a temperature below its crystallization range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI"). CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% (that is, 25% on each side) of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions generally represent a trivial portion of the resin of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurement.

From the weight fraction versus composition distribution curve the CDBI is

determined by establishing what weight percent of the sample has a comonomer content within 25% each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

The resins of the present invention have CDBI's generally in the range of greater than 70 to 98%, usually in the range of 75-98% and most typically in the range of 85-95%. Obviously, higher or lower CDBI's may be obtained using other catalyst systems with changes in the operating conditions of the process employed.

A class of highly active olefin catalysts known as metallocenes may be used in the preparation of these VLDPE copolymers. These catalysts, particularly those based on Group IVB transition metals such as zirconium, titanium and hafnium, show extremely high activity in ethylene polymerization. Metallocenes are well known especially in the preparation of polyethylene and copolyethylene-alpha-olefins. For the purposes of this patent specification the term "metallocene" is herein defined to contain one or more cyclopentadienyl moiety in combination with a transition metal of the Periodic Table of Elements. The metallocene catalyst component is represented by the general formula $(C_p)_mMR_nR'_p$ wherein C_p is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IV, V or VI 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 in the polymerization process of this invention. Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in the disclosure of U.S. Patent No. 4,871,705 to Hoel, U.S. Patent No. 4,937,299 to Ewen, et al. and EP-A-0 129 368 published July 26, 1989, and U.S. Patent Nos. 5,017,714 and 5,120,867 to Welborn, Jr. all of which are fully incorporated herein by reference. These publications teach the structure of the metallocene catalysts and include alumoxane as the cocatalyst. There are a variety of methods for preparing alumoxane one of which is described in U.S. Patent 4,665,208. Other cocatalysts may be used with metallocenes, such as trialkylaluminum compounds; or ionizing ionic activators or compounds such as, tri (n-butyl) ammonium tetra (pentaflurophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing ionic compound. Such compounds are

described in EP-A-0 520 732, EP-A-0 277 003 and EP-A-0 277 004 both published August 3, 1988, and U.S. Patent Nos. 5,153,157 and 5,198,401 and are all herein fully incorporated by reference. Further, the metallocene catalyst component can be a monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane or an ionic activator to form an active polymerization catalyst system to produce polymers useful in this present invention. These types of catalyst systems are described in, for example, PCT International Publications WO 92/00333 published January 9, 1992, U.S. Patent Nos. 5,096,867 and 5,055,438, EP-A-0 420 436 and WO 91/ 04257 all of which are fully incorporated herein by reference. In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbollides in combination with a transition metal. Additionally it is not beyond the scope of this invention that the catalysts and catalyst systems may be those described in U.S. Patent No. 5,064,802 and PCT publications WO 93/08221 and WO 93/08199 published April 29, 1993 all of which are herein incorporated by reference. All the catalyst systems described above may be, optionally, prepolymerized or used in conjunction with an additive or scavenging component to enhance catalytic productivity.

Utilizing a metallocene catalyst, the VLDPE copolymers useful as the low melting polymers of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

A slurry polymerization process generally uses super-atmospheric pressures and temperatures in the range of 40-100°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 an alkane, 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.

Alternatively, the VLDPE copolymer component 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 50°C-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. Ethylene, comonomer, hydrogen and an inert

diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperatures of 50°C-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other impurities. Polymer product can be withdrawn continuously or semicontinuously 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 VLDPE copolymers of the present invention can also be produced in accordance with a high pressure process by polymerization ethylene in combination with other monomers such as butene-1, hexene-1, octene-1, or 4-methylpentene-1 in the presence of the catalyst system comprising a cyclopentadienyl-transistion metal compound and an alumoxane compound and the catalyst systems described above. It is important, in the high-pressure process, that the polymerization temperature be above 120°C but below the decomposition temperature of the polymer product and that the polymerization pressure be above 500 bar (kg/cm2). In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in the process of this invention.

The low to medium density ethylene polymer with which the VLDPE is blended to form the improved films of this invention may be characterized by a density in the range of from above 0.910 to 0.935 g/cm^3 and generally exhibit a higher melt index than the VLDPE component, i.e., a MI above 3, preferably above 5.0 and up to 20, a molecular weight distribution above 3.5 and a compositional distribution breadth index of less than 70%, usually less than 55%. These materials may be prepared by conventional high pressure polymerization processes using free radical catalyst systems. Preferred polymers are low density polyethylene as well as low density copolymers of ethylene with up to 30 mole % of a comonomer such as propylene, vinyl acetate, acrylic acid and lower alkyl esters of acrylic acid. Preferred LDPE polymers have a preferred density in the range of from above .915 to .930 g/cm^3 and a preferred MI in the range of from 5 to 15.

The blend composition of the monolayer film contains from 25 to 90% by

weight of the VLDPE and correspondingly from 75 to 10% by weight of the low to medium density ethylene polymer, each based on the total weight of polymer present in the composition. More preferred levels range from 50 to 80% by weight of the VLDPE component, most preferably from 50 to 70% by weight of the VLDPE component.

As indicated above, the present invention also provides an embodiment wherein films of ABA construction may be prepared wherein the above described blend comprises the skin or A layers, and a different polyolefin polymer comprises the core or B layer. Because of the extremely good physical properties of films prepared from the VLDPE/LDPE blend material and particularly because of the enhanced noise reduction and softness properties of such films, such an ABA construction permits the utilization as the B core layer a material which might not otherwise be desirable for the fabrication of back sheet material due to excessive noise, poor feel or other factors. Such materials include conventional high density polyethylene having a density in the range from .940 to .980 g/cm^3 and particularly scrap high density polyethylene which has been recycled and reclaimed, such as that reclaimed from milk or soft drink containers. Thus the invention provides for cost effective re-use of such materials and environmental benefits. The core layer may also contain minor amounts of the composition of the outer or skin layers so occasioned by the recycle of scrap or trim film back into the extruder to be mixed with the polymer used to prepare the core layer.

The films of the present invention may be fabricated using cast extrusion techniques well known in the art. For example, the monolayer film may be prepared by forming a uniform mixture of the polymer components and any other additives in a compounder extruder, extruding the mixture through a flat die at a temperature above the melting points of the polymer components, e.g. at temperatures from about 245°C (475°F) to about 290°C (550°F), to form a web, and casting the web on a chilled, smooth or patterned surface casting roll. For many applications it is preferred to emboss the cast film to produce a roughened pattern on the film surface such as disclosed in U.S. Patent 4,436,520 to reduce the surface gloss of the film. This embossing may be carried out using a casting roll having a patterned surface and a pressure roll wherein the web is passed through the nip of these rolls. The resulting film is then cooled and wound, or the film may be further oriented by drawing in one or two mutually perpendicular directions by techniques well known in the art.

Where the film is a laminar film of ABA construction, the film may be

prepared by the technique described above using coextrusion techniques. Thus the polymer forming the core layer, i.e., HDPE, is coextruded with the two outer layers using a multiple die coextruder, or molten layers of the outer layers may be applied to the surfaces of an extruded cast film of the core layer.

A particular advantage associated with films prepared using the polymer blend components of this invention is that the film exhibits improved draw resonance properties during the production processing steps.

The films of this invention may have an overall film thickness in the range of from about 12 to about 52 μ (0.50 to 2 mil), more preferably from about 19 μ to about 40 μ (0.75 to 1.5 mil). Where ABA type laminar films are prepared, the core B layer may constitute from 20 to 75% by weight of the total film, more preferably from 25 to 60% by weight of the total film.

The polymer components used to fabricate the films of the present invention may also contain effective amounts of other additives normally included in such compositions. These include slip agents such as talc, antioxidants, fillers, dyes, pigments, radiation stabilizers, plasticizers and like additives.

For diaper backing applications, it is preferred to incorporate into the composition a light-colored pigment masterbatch concentrate (MB) composition which may contain a mixture of pigment, antioxidant, dispersant and other additives dispersed in a suitable olefin polymer matrix.

EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered as related to actual tests performed in the practice of this invention, and illustrate the benefits of this present invention and not intended as a limitation on the scope of the invention.

EXAMPLE I

A monolayer film was prepared by mixing a polymer formulation having the composition set forth below in a 8.89 cm (3 1/2 inch) Black Clawson extruder and melt extruding a web of the polymer at a temperature of approximately 260°C (500°F) vertically down into the nip between an embossing chill roll having a matte surface and a smooth surface rubber roll. The chill and rubber rolls were maintained at a temperature of 130 to 140°C and 50 to 60°C respectively and at a contact pressure of 276 kPa (40 psi) to yield film material exiting the roll nip having an average thickness of 31 μ to 33 μ (1.2 to 1.3 mil). The resulting film was picked off the chill roll by a secondary chill roll maintained at 60°C, taken up

and wound at an initial speed of 254 cm/sec (500 ft/min) to yield a finished film having a thickness in the order of 20 μ to 25 μ (0.8 to 1.0. mil).

Once the system had stabilized under the aforementioned conditions, the rate of take-up (draw line speed) was slowly increased by increasing the speed of the take-up rolls and each film observed for the appearance of draw resonance as evidenced by light and dark bands running across the film.

The composition of the monolayer film prepared above was as follows:

a) 70% by weight of a very low density polyethylene based on a copolymer of ethylene and less than 10 mole% butene-1 having a density of 0.88 g/cm^3 and a Melt Index of 2.0 dg/min.;

b) 25% by weight of a high pressure low density polyethylene homopolymer having a density of 0.917 g/cm^3 and a Melt Index of 12.0 dg/min.;

c) 5% by weight of a masterbatch white pigment concentrate dispersed in polyethylene component (b).

CONTROL A

A control monolayer film was prepared as set forth in Example 1 with the exception that a linear low density polyethylene was substituted for VLDPE component (a) and in the same amount. This LLDPE was a copolymer of ethylene and 3.5 mole% of hexene-1 having a density of 0.918 and a Melt Index 2.0

Films made from the composition of Example 1 and Control A were drawn at an initial rate of 254 cm/sec (500 ft/min) which speed was increased gradually to over 305 cm/sec (600 ft/min) The film of Example 1 drew down to a thickness of 14 μ (0.55 mil) at a speed of 319 cm/sec (627 ft/min) prior to breaking, with no indication of draw resonance up to the point where the film tore off. The Control A film exhibited draw resonance prior to reaching a draw speed of 305 cm/sec (600 ft/min).

EXAMPLES 2 AND 3

Example 1 was repeated using two additional formulations wherein the film components used in Example 1 were present at the following levels:

Ex. 2 -	(a) VLDPE	- 50% by weight
	(b) LDPE	- 45% by weight
	(c) Pigment concentrate	- 5% by weight
Ex. 3 -	(a) VLDPE	- 30% by weight
	(b) LDPE	- 65% by weight
	(c) Pigment concentrate	- 5% by weight

Films were drawn at a rate of 254 cm/sec (500 ft/min). Physical properties

of these films as well as the Control A and Example 1 film (also drawn at 254 c/sec (500 ft/min.)) are shown in Table 1.

TABLE 1

Film	Control A	EX. 1	EX. 2	EX. 3
YAG_1 (mil)	1.20	1.23	1.25	1.25
YAG_1 (μ)	30.48	31.24	31.75	31.75
Dart Impact (g)	166	338	262	230
TD_2 Ult. Tens. (g/in)	1740	2672	2117	1754
TD_2 Ult. Tens. (g/cm)	685.0	1052.0	833.5	690.6
TD Ult. Elon. (%)	671	733	698	676
TD Sec. Mod. (psi)	NT*	12,430	14,170	14,570
TD Sec. Mod. (kPa)	NT*	85705	97702	100460
MD_3 Ult. Elong. (%)	482	574	471	416
MD Ult. Tens. (g/in)	2148	3093	2484	2133
MD Ult. Tens. (g/cm)	845.7	1218	978	840
MD Sec. Mod. (psi)	NT*	11,910	14,070	13,820
MD Sec. Mod. (kPa)	NT*	82120	97013	95289

1 YAG - Average film thickness calculated based on film weight and polymer density

2 TD - Transverse direction

3 MD - Machine direction

NT* - Not tested

EXAMPLES 4, 5 AND 6

Three additional formulations were prepared and processed into monolayer film by the method set forth in Example 1. Components were blended at the following levels:

a) VLDPE* - 67% by weight

b) LDPE (Same as Ex. 1) - 28% by weight

c) Pigment Concentrate - 5% by weight

*In Example 4, the VLDPE used was a copolymer of ethylene and butene-1 having a melt index of 2.2 and a density of 0.885.

In Example 5, the VLDPE used was a copolymer of ethylene and hexene-1 having a melt index of 2.2 and a density of 0.889.

In Example 6, the VLDPE used was a copolymer of ethylene and hexene-1 having a melt index of 2.2 and a density of 0.906.

CONTROL B

Example 1 as repeated with the same level of ingredients as in Examples 4-6 with the exception that a linear low density polyethylene (LLDPE) was substituted for the VLDPE and in the same amount. The LLDPE used in this Control was a copolymer of ethylene and octene-1 having a Melt Index of 2.5 and a density of 0.935.

Films made from the formulation of Examples 4-6 and Control B were cast and embossed to yield an average post emboss film gauge of 30.5 μ (1.2 mils) and drawn at an initial line speed of 254 cm/sec (500 ft/min). For each film, the line speed was gradually increased until the film tore. Table 2 reports the melt temperature of the composition exiting the extruder, the observation of Draw Resonance, the film thickness just before the film tore and the film speed at the time of tear.

TABLE 2

	Melt Temperature		Draw Resonance	Film Thickness at Tear		Speed at Tear	
	(°C)	(°F)		(μ)	(mil)	cm/sec	ft/min
EX. 4	263	506	None	19.1	0.75	411.5	810
EX. 5	262	504	None	14.5	0.57	541.5	1066
EX. 6	265	509	None	17.8	0.70	443.8	872
Control B	267	513	Yes (Prior to 305 cm/sec (600 ft/min))	17.0	0.67	467.4	920

As shown by the data in Table 2, none of the films made using formulations within the scope of this invention exhibited draw resonance prior to film tear, whereas the formulation of Control B exhibited draw resonance prior to draw speeds of 305 cm/sec (600 ft/min).

As indicated above, this invention also provides for laminar films of ABA construction wherein the A, or skin layers, comprise the blends of this invention

and the B, or core layer, comprises a different polyolefin such as high density polyethylene. The following example illustrates the preparation of such a laminar film.

EXAMPLE 7

An ABA laminar film was prepared by coextruding a ground up, reclaimed high density polyethylene having a density of .9616 g/cm^3 and the composition of Example 1 containing a mixture of 70% by weight of VLDPE, 25% by weight of LDPE and 5% by weight of pigment concentrate. These materials were coextruded at 270.6 to 294.4°C (519 to 526°F) through a coextrusion die at a rate of 101.4 kg/hr (400 lbs/hr) in a configuration such that the HDPE formed the core B layer and the VLDPE mixture formed the skin A layers. The resultant film had a thickness of 30.5 μ (1.2 mil) with the core layer having thickness of 7.62 μ (0.30 mil)and each skin layer a thickness of 11.4 μ (0.45 mil)

CONTROL C

Example 7 was repeated except that a linear low density polyethylene (based on a copolymer of ethylene and 1-octene) was substituted for the VLDPE component of the skin layer formulation. The LLDPE had a melt index of 2.0 and a density of 0.918. The resulting film had a thickness of 30.5 μ (1.2 mil), with a core layer thickness of 7.62 μ (0.30 mil) and skin layer thickness of 11.4 μ (0.45 mil) each.

Properties of the resulting films are shown in Table 3.

TABLE 3

Film	EX. 7	Control C
CD-10%	562	672
TD-Break (g/in)	2668	2247
TD-Break (g/cm)	1050.4	884.6
TD-Elong (%)	702	693
MD-Break (g/in)	3023	1926
MD-Break (g/cm)	1190.2	758.3
MD-Elong (%)	583	396
Dart Impact (g)	198	123

Note: CD-10% - Tensile strength at 10% Elongation
TD-Break - Tensile strength at break(transverse direction)
TD-Elong - Elongation at break (transverse direction)
MD - Machine direction

As shown in Table 3, laminar films of the present invention exhibit markedly better physical and mechanical properties when compared with a comparable film containing a LLDPE instead of VLDPE in the skin layers.

CLAIMS

We Claim.

1. A polymer composition comprising a mixture of:

a) 25 to 90% by weight, based on polymer content, of a copolymer of ethylene and a C_4 to C_{20} alpha-monoolefin comonomer, said copolymer having a density of from 0.88 to 0.925 g/cm^3, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution of no greater than 3.5 and a compositional distribution breath index greater than 70 percent, and

b) 10 to 75% by weight, based on polymer content, of a low to medium density ethylene polymer having a density in the range of from 0.910 to 0.935 g/cm3, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution above 3.5 and a compositional breath index of less than 70%.

2. A method of reducing draw resonance during the production of polyolefin film material comprising:

i) forming a polymer mixture in accordance with claim 1;

ii) melt extruding said mixture at a temperature of up to 288°C into a nip formed by a casting roll and a pressure roll; and

iii) taking-up said film from said casting roll at a linear speed in excess of 254 cm/sec.

3. A film prepared from the composition of claim 1 or the method of claim 2.

4. The composition of any of the preceding claims containing from 50 to 80% by weight of component (a) and from 20 to 50% by weight of component (b).

5. The composition of any of the preceding wherein component (b) is a low density ethylene polymer having a density of above 0 915 g/cm3.

6. The composition of any of the preceding claims wherein said component (b) is an ethylene polymer having a melt index of from 5 to 15 dg/min.

7. The composition of any of the preceding claims wherein said ethylene copolymer (a) contains from 4 to 15 mole percent of said comonomer.

8. The composition of any of the preceding claims wherein said component (a) is a terpolymer comprising said copolymer of ethylene and said C_4 to C_{20} alpha-mono-olefin and an additional C_4 to C_{20} alpha-olefin different from said alpha-mono-olefin.

9. The film of claim 2 or 3 having a thickness in the range of from 12 μ to 52 μ.

10. The film of claim 2 or 3 which is a monolayer film.

11. The film of claim 2 or 3 which is a laminar film of ABA construction wherein each A layer comprises said mixture and said B layer comprises a different polyolefin composition.

12. The film of claim 11 wherein said B layer is HDPE or recycled HDPE.

13. The film of claim 11 wherein said B layer comprises from 20 to 75% by weight of said film.

14. An article of manufacture made from the film of claim 2 or 3.

15. The process of claim 2 wherein said melt extrusion temperature is at least 246°C.

16. The process of claim 2 wherein said casting roll has an embossed surface to provide a film having a matte surface.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 93/08586

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L23/04 C08J5/18

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08L C08J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 244 982 (EL PASO PRODUCTS) 11 November 1987 see page 2, line 1 - line 50	1-10
Y	WO,A,90 03414 (EXXON CHEMICAL PATENTS) 5 April 1990 Abstract see page 2, line 3 - page 5, line 22	1-10
A	EP,A,0 461 848 (MITSUI PETROCHEMICAL INDUSTRIES) 18 December 1991 see claim 1	2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 December 1993	13. 01. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Goovaerts, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
information on patent family members

Inter. nal Application No
PCT/US 93/08586

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0244982	11-11-87	US-A-	5051297	24-09-91
		US-A-	5066724	19-11-91
WO-A-9003414	05-04-90	AU-B-	615804	10-10-91
		AU-A-	4338089	18-04-90
		EP-A-	0389611	03-10-90
		JP-T-	3502710	20-06-91
EP-A-0461848	18-12-91	JP-A-	4103649	06-04-92
		JP-A-	4120144	21-04-92
		CN-A-	1057276	25-12-91
		JP-A-	4226141	14-08-92
		US-A-	5262228	16-11-93

Form PCT/ISA/210 (patent family annex) (July 1992)

FORM PTO 1449 (modified) LIST OF REFERENCES CITED BY APPLICANT	Atty. Docket No. C-40121-AU	Serial No. 08/544,497
	Applicant: Pak-Wing Steve Chum et al.	
	Filing Date: 10-18-95	Group: 1505

U.S. PATENT DOCUMENTS

Examiner Initial		Document Number	Date	Name	Class	Sub-class	Filing Date If Appropriate
DW	AA	5,395,471	03-07-95	Obijeski et al.	156	244.11	
	AB	5,395,810	03-07-95	Shamshoum et al.	502	113	
	AC	5,408,004	04-18-95	Lai et al.	525	240	
DW	AD	5,444,145	08-22-95	Brant et al.	526	348.3	
	AE						
	AF						
	AG						
	AH						
	AI						
	AJ						
	AK						

FOREIGN PATENT DOCUMENTS

		Document Number	Date	Country	Class	Sub-class	Translation	
DW	BA	WO 94/12568 A1	06-09-94	PCT	C08L	23/08		
	BB	WO 95/13321 A1	05-18-95	PCT	C08L	23/04		
	BC	WO 93/13143 A1	07-08-93	PCT	C08F	10/02		
	BD	WO 93/03093 A1	02-18-93	PCT	C08L	23/04		
DW	BE							

OTHER REFERENCES *(Including Author, Title, Date, Pertinent Pages, Etc.)*

DW	C A		"A Review of High Resolution Liquid ^{13}Carbon Nuclear Magnetic Resonance Characterizations of Ethylene-Based Polymers", pp. 201-317, by James C. Randall
	C B		ACS Symposium Series, no. 142, pp. 94-118. " Characterization of Long-Chain Branching in Polyethylenes Using High -Field Carbon-13 NMR", by J. C. Randall
	C C		SPE Regional Technical Conference, Quaker Square Hilton, Akron, Ohio, October 1-2, (1985), pp. 107-119, "The Role of Comonomer Type and Distribution in LLDPE Product Performance", by L. D. Cady
	C D		Journal of Polymer Science:Polymer Physics Edition, vol. 20, pp. 441-455 (1982), "Determination of Branching Distributions in Polyethylene and Ethylene Copolymers", by L. Wild, T. R. Ryle, D. C. Knobeloch, and I. R. Peat
	C E		Antec 93, pp. 58-62, " Flexomer Polyolefins, A Unique Class of Ethylene Copolymers for Low Temperature Film Applications", by D. C. Eagar, G. E. Ealer, S. A. Bartocci and D. M. Kung
DW	C F		Worldwide Metallocene Conference MetCon '94, May 25-27, (1994), "Improved Processing and Performance Balance of Polyethylene Resins Using Metallocene Catalyst Technology", by Mark A. Wendorf

EXAMINER David W/u	DATE CONSIDERED 8-2-96

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

05/07/95 XR 5,395,471

US005395471A

United States Patent [19]

Obijeski et al.

[11] Patent Number: 5,395,471

[45] Date of Patent: Mar. 7, 1995

[54] **HIGH DRAWDOWN EXTRUSION PROCESS WITH GREATER RESISTANCE TO DRAW RESONANCE**

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[21] Appl. No.: **84,054**

[22] Filed: **Jun. 29, 1993**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236, and a continuation-in-part of Ser. No. 939,281, Sep. 2, 1992, Pat. No. 5,278,272, and a continuation-in-part of Ser. No. 55,063, Apr. 28, 1993.

[51] **Int. Cl.**[6] **B29C 47/02**

[52] **U.S. Cl.** **156/244.11**; 156/244.24; 526/348; 526/348.5

[58] **Field of Search** 156/244.11, 244.24; 526/127, 132, 150, 152, 160, 170, 336, 348, 348.2, 348.3, 348.4, 348.5, 348.6, 516

[56] **References Cited**

U.S. PATENT DOCUMENTS

Re. 33,683	9/1991	Allen et al. .
3,247,290	4/1966	Werkman et al. .
3,371,464	3/1968	Swick .
3,456,044	7/1969	Pahlke .
3,491,073	1/1970	Marinak .
3,555,604	1/1971	Pahlke .
3,645,992	2/1972	Elston .
3,914,342	10/1975	Mitchell .
4,011,384	3/1977	Baxmann et al. .
4,076,698	2/1978	Anderson et al. .
4,205,021	5/1980	Morita et al. .
4,259,468	3/1981	Kajiura et al. .
4,302,566	11/1981	Karol et al. .
4,303,710	12/1981	Bullard et al. .
4,303,771	12/1981	Wagner et al. .
4,328,328	5/1982	Minami et al. .
4,339,493	7/1982	Weiner .
4,339,496	7/1982	Weiner .
4,339,507	7/1982	Kurtz et al. .
4,340,640	7/1982	Weiner .
4,340,641	7/1982	Weiner .
4,346,834	8/1982	Mazumdar .
4,348,346	9/1982	Thompson .
4,349,648	9/1982	Jorgensen et al. .
4,352,849	10/1982	Mueller .
4,354,009	10/1982	Goeke et al. .
4,359,495	11/1982	Schroeder et al. .
4,359,553	11/1982	Edwards .
4,359,561	11/1982	Fraser et al. .
4,363,904	12/1982	Fraser et al. .
4,365,044	12/1982	Liu .
4,367,256	1/1983	Biel .
4,370,456	1/1983	George .
4,378,451	3/1983	Edwards .
4,379,197	4/1983	Cipriani et al. .
4,380,567	4/1983	Shigemoto .

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

2123747A	2/1984	United Kingdom .
9106426	5/1991	WIPO .

OTHER PUBLICATIONS

Roberts et al., *ANTEC Proceedings '85*, "New Process for the Reduction of Draw Resonance in Melt Embossing and Extrusion Coating", pp. 104–107.

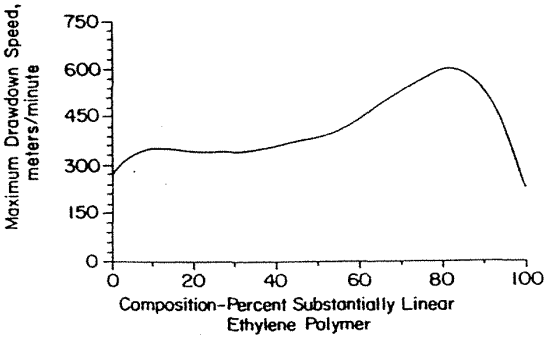
(List continued on next page.)

Primary Examiner—Caleb Weston

[57] **ABSTRACT**

A process for extruding a thermoplastic composition at higher drawdown rates with less neck-in and greater resistance to draw resonance as well as processes for extrusion coating a substrate and for making an extrusion-cast film are disclosed. The thermoplastic composition is made of at least one substantially linear ethylene polymer used alone or in combination with at least one high-pressure ethylene polymer and/or with at least one heterogeneous linear olefin polymer.

19 Claims, 1 Drawing Sheet



U.S. PATENT DOCUMENTS

4,383,095	5/1983	Goeke et al. .
4,387,185	6/1983	Schroeder et al. .
4,390,677	6/1983	Karol et al. .
4,399,180	8/1983	Briggs .
4,405,774	9/1983	Miwa et al. .
4,410,649	10/1983	Cieloszyk .
4,418,114	11/1983	Briggs et al. .
4,424,138	1/1984	Candlin et al. .
4,427,573	1/1984	Miles et al. .
4,427,833	1/1984	Edwards .
4,429,079	1/1984	Shibata et al. .
4,438,238	3/1984	Fukushima et al. .
4,438,243	3/1984	Kashiwa et al. .
4,452,958	6/1984	Chester et al. .
4,454,281	6/1984	Heitz et al. .
4,461,792	7/1984	Anthony .
4,463,153	7/1984	Mizutani et al. .
4,464,426	8/1984	Anthony .
4,467,065	8/1984	Williams et al. .
4,482,687	11/1984	Noshay et al. .
4,485,217	11/1984	Gunter et al. .
4,486,377	12/1984	Lucchesi et al. .
4,486,552	12/1984	Neimann .
4,486,579	12/1984	Machon et al. .
4,505,970	3/1985	Craver .
4,510,303	4/1985	Oda et al. .
4,513,038	4/1985	Anthony .
4,514,465	4/1985	Schoenberg .
4,519,968	5/1985	Klaus et al. .
4,526,919	7/1985	Edwards .
4,528,312	7/1985	Edwards .
4,530,914	7/1985	Ewen et al. .
4,532,189	7/1985	Mueller .
4,542,886	9/1985	Yoshimura et al. .
4,544,762	10/1985	Kaminsky et al. .
4,547,555	10/1985	Cook et al. .
4,551,380	11/1985	Schoenberg .
4,563,504	1/1986	Hert et al. .
4,564,559	1/1986	Wagner .
4,568,713	2/1986	Hansen et al. .
4,587,318	5/1986	Inoue et al. .
4,588,650	5/1986	Mientus et al. .
4,588,794	5/1986	Oda .
4,593,009	6/1986	Nowlin .
4,597,920	7/1986	Golike .
4,598,128	7/1986	James et al. .
4,599,391	7/1986	Yamamoto et al. .
4,599,392	7/1986	McKinney et al. .
4,608,221	8/1986	Kurtz et al. .
4,613,547	9/1986	Wagner et al. .
4,617,241	10/1986	Mueller .
4,618,662	10/1986	Nowlin .
4,624,991	11/1986	Haas .
4,626,467	12/1986	Hostetter .
4,626,574	12/1986	Cancio et al. .
4,629,771	12/1986	Candlin et al. .
4,640,856	2/1987	Ferguson .
4,649,001	3/1987	Nakamura et al. .
4,666,772	5/1987	Schinkel et al. .
4,666,999	5/1987	Cook et al. .
4,668,463	5/1987	Cancio et al. .
4,668,575	5/1987	Schinkel et al. .
4,668,650	5/1987	Lo et al. .
4,668,752	5/1987	Tominari et al. .
4,672,096	6/1987	Nowlin .
4,676,922	6/1987	Sommer .
4,677,087	6/1987	Lo et al. .
4,690,991	9/1987	Seppl .
4,690,992	9/1987	Grubbs et al. .
4,692,386	9/1987	Schinkel et al. .
4,710,538	12/1987	Jorgensen .
4,716,207	12/1987	Cozewith et al. .
4,719,193	1/1988	Levine et al. .
4,720,427	1/1988	Clauson et al. .
4,722,971	2/1988	Datta et al. .
4,724,185	2/1988	Shah .
4,732,882	3/1988	Allen et al. .
4,737,391	4/1988	Lustig et al. .
4,742,138	5/1988	Kageyama .
4,755,403	7/1988	Ferguson .
4,755,419	7/1988	Shah .
4,762,898	8/1988	Matsuura et al. .
4,764,549	8/1988	Greenhalgh et al. .
4,767,485	8/1988	Michiels .
4,775,710	10/1988	Dunski et al. .
4,780,264	10/1988	Dohrer et al. .
4,788,232	11/1988	Needham .
4,789,714	12/1988	Cozewith et al. .
4,792,595	12/1988	Cozewith et al. .
4,798,081	1/1989	Hazlitt et al. .
4,801,486	1/1989	Quacquarella et al. .
4,803,253	2/1989	McDaniel et al. .
4,808,635	2/1989	Nguyen .
4,820,557	4/1989	Warren .
4,820,589	4/1989	Dobreski et al. .
4,824,889	4/1989	Mostert .
4,826,939	5/1989	Stuart .
4,830,926	5/1989	Mostert .
4,833,017	5/1989	Benoit .
4,834,947	5/1989	Cook et al. .

(List continued on next page.)

U.S. PATENT DOCUMENTS

4,842,187	6/1989	Janocha et al. .
4,842,930	6/1989	Schinkel .
4,842,951	6/1989	Yamada et al. .
4,857,611	8/1989	Durand et al. .
4,859,379	8/1989	Chiang .
4,863,769	9/1989	Lustig et al. .
4,863,784	9/1989	Lustig et al. .
4,865,902	9/1989	Golike et al. .
4,874,820	10/1989	Cozewith et al. .
4,876,321	10/1989	Lo et al. .
4,882,406	11/1989	Cozewith et al. .
4,883,853	11/1989	Hobes et al. .
4,886,690	12/1989	Davis et al. .
4,888,318	12/1989	Allen et al. .
4,892,911	1/1990	Genske .
4,921,920	5/1990	Collomb-Ceccarini et al. .
4,923,750	5/1990	Jones .
4,925,728	5/1990	Crass et al. .
4,927,708	5/1990	Herran et al. .
4,935,474	6/1990	Ewen et al. .
4,937,299	6/1990	Ewen et al. .
4,952,451	8/1990	Mueller .
4,957,790	9/1990	Warren .
4,959,436	9/1990	Cozewith et al. .
4,963,388	10/1990	Benoit .
4,963,419	10/1990	Lustig et al. .
4,963,427	10/1990	Botto et al. .
4,966,951	10/1990	Benham et al. .
4,967,898	12/1990	Lustig et al. .
4,968,765	11/1990	Yagi et al. .
4,975,315	12/1990	Bolthe et al. .
4,976,898	12/1990	Lustig et al. .
4,977,022	12/1990	Mueller .
4,981,760	1/1991	Naito et al. .
4,981,826	1/1991	Speca .
4,983,447	1/1991	Crass et al. .
4,987,212	1/1991	Morterol et al. .
4,988,465	1/1991	Lustig et al. .
4,996,094	2/1991	Dutt .
5,006,396	4/1991	VanBortel et al. .
5,006,398	4/1991	Banerji .
5,013,801	5/1991	Cozewith et al. .
5,015,511	5/1991	Treybig et al. .
5,015,749	5/1991	Schmidt et al. .
5,019,315	5/1991	Wilson .
5,024,799	6/1991	Harp et al. .
5,025,072	6/1991	Nowlin et al. .
5,026,798	6/1991	Canich .
5,032,463	7/1991	Smith .
5,041,316	8/1991	Parnell et al. .
5,041,584	8/1991	Crapo et al. .
5,041,585	8/1991	Deavenport et al. .
5,043,040	8/1991	Butler .
5,047,468	9/1991	Lee et al. .
5,055,328	10/1991	Evert et al. .
5,055,338	10/1991	Sheth et al. .
5,055,438	10/1991	Canich .
5,055,533	10/1991	Allen et al. .
5,055,534	10/1991	Theobald .
5,059,481	10/1991	Lusting et al. .
5,064,796	11/1991	Speca .
5,064,802	11/1991	Stevens et al. .
5,068,489	11/1991	Edwards et al. .
5,073,452	12/1991	Satou et al. .
5,073,599	12/1991	Genske .
5,075,143	12/1991	Bekele .
5,082,908	1/1992	Imai et al. .
5,084,039	1/1992	Cancio et al. .
5,084,540	1/1992	Albizzati et al. .
5,084,927	2/1992	Parkevich .
5,089,321	2/1992	Chum et al. .
5,106,545	4/1992	Warren .
5,106,688	4/1992	Bradfute et al. .
5,112,674	5/1992	German et al. .
5,206,075	4/1993	Hodgson, Jr. .
5,218,071	6/1993	Tsutsui et al. .
5,241,031	8/1993	Mehta .

OTHER PUBLICATIONS

Lucchesi et al., *Plastics Engineering,* "Reducing draw resonance in LLDPE film resins", pp. 87–90, May 1985.

ANTEC Proceedings 1989, "Resistance to Draw Resonance of Linear Low Density Polyethylene Through Improved Resin Design", pp. 28–30.

Randall, *ACS Symposium Series No. 142,* "Polymer Characterization by ESR and NMR", pp. 93–117 (1980).

M. Shida et al., *Polymer Engineering Science,* vol. 17, No. 11, "Correlation of Low Density Polyethylene Rheological Measurements with Optical and Processing Properties" pp. 769–774 (1977).

John Dealy, *Rheometers for Molten Plastics,* Van Nostrand Reinhold Co., pp. 97–99, (1982).

S. Lai et al., *ANTEC '93 Proceedings,* "Dow Constrained Geometry Catalyst Technology (CGCT)–New

(List continued on next page.)

OTHER PUBLICATIONS

Rules for Ethylene α–Olefin Interpolymers–Controlled Rheology Polyolefins", New Orleans, La., pp. 1182–1192, (May 1993).

Ramamurthy, *Journal of Rehology,* "Wall Slip in Viscous Fluids and Influence of Materials of Construction", John Wiley & Sons, 30(2), pp. 337–357, (1986).

Wild et al., *Journal of Polymer Science, Poly. Phys. Ed.,* "Determination of Branching Distributions in Polyethylene and Ethylene Copolymers", John Wiley & Sons, vol. 20, p. 441 (1982).

Williams and Ward, *Journal of Polymer Science: Polymer Letters,* vol. 6, "The Construction of a Calibration Curve for Gel Permeation Chromatography using Polystyrene Fractions", pp. 621–627, (1968).

Journal of Polymer Science, Part A, vol. 1 (pp. 2869–2880 (1963)), "Long–Chain Branching Frequency in Polyethylene" by J. E. Guillet.

Polymer Preprints, Amer. Chem. Society, vol. 12, No. 1, pp. 277–281 (Mar. 1971), "Evidence of Long–Chain Branching in High Density Polyethylene" by E. E. Drott and R. A. Mendelson.

Journal of the American Chemical Society, 98:7, pp. 1729–1742 (Mar. 31, 1976) "Structure and Chemistry of Bis(cyclopentadienyl)–MLn Complexes" by Joseph W. Lauher and Roald Hoffman.

Polymer Engineering and Science, vol. 16, No. 12, pp. 811–816 (Dec. 1976), "Influence of Long–Chain Branching on the Viscoelastic Properties of Low–Density Polyethylenes" by L. Wild, R. Ranganath, and D. Knobeloch.

Angew. Chem. Int. Ed. Engl. pp. 630–632 (1976) vol. 15, No. 10, "Halogen–Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature" by Arne Andresen et al.

Advances in Organometallic Chemistry, pp. 99–148, vol. 18, (1980) "Ziegler–Natta Catalysis" by Hansjorg Sinn and Walter Kaminsky.

Angew. Chem. Int. Ed. Engl., pp. 390–393, vol. 19 No. 5 (1980) "Living Polymers' on Polymerization with Extremely Productive Ziegler Catalysts" by Hansjorg Sinn, Walter Kaminsky, Hans–Jurgen Vollmer, and Rudiger Woldt.

Polymer Bulletin, 9, pp. 464–469 (1983) "Halogen Free Soluble Ziegler Catalysts with Methylalumoxan as Catalyst" by Jens Herwig and Walter Kaminsky.

Makromol. Chem., Rapid Commun., 4, pp. 417–421 (1983) "Bis(cyclopentadienyl)zirkon–Verbingungen und Aluminoxan als Ziegler–Katalysatoren fur die Polymerisation und Copolymerisation von Olefinen" by Walter Kaminsky et al.

ANTEC Proceedings, pp. 306–309 (1983), "Analysis of Long Chain Branching in High Density Polyethylene" by J. K. Hughes.

Makromol. Chem., Rapid Commun., (5) pp. 225–228 (1984) "Influence of hydrogen on the polymerization of ethylene with the homogeneous Ziegler system bis(cyclopentadienyl)zirconiumdichloride/aluminoxane" by Walter Kaminsky et al.

Journal of Polymer Science Polymer Chemistry Edition, pp. 2117–2133 (1985) vol. 23, "Homogeneous Ziegler–Natta Catalysis. II. Ethylene Polymerization by IVB Transition Metal Complexes/Methyl Aluminoxane Catalyst Systems" by E. Giannetti and R. Mazzocchi.

Journal of Applied Polymer Science, pp. 3751–3765 (1985) vol. 30, "On the Effects of Very Low Levels of Long Chain Branching on Rheological Behavior in Polyethylene" by B. H. Bersted.

Journal of Polymer Science: Polymer Chemistry Edition, pp. 2151–2164 (1985) vol. 23, "Ethylene Propylene Diene Terpolymers Produced with a Homogeneous and Highly Active Zirconium Catalyst" by Walter Kaminsky et al.

The Society of Rehology, pp. 337–357 (1986) vol. 30, "Wall Slip in Viscous Fluids and Influence of Materials of Construction" by A. V. Ramamurthy.

Makromol. Chem., Macromol. Symp., 4, pp. 103–118 (1986) "Elastomers By Atactic Linkage of α–Olefins Using Soluble Ziegler Catalysts" by W. Kaminsky and M. Schlobohm.

Journal of Rheology, 31 (8) pp. 815–834 (1987) "Wall Slip and Extrudate Distortion in Linear Low–Density Polyethylene" by D. Kalika and M. Denn.

Makromol. Chem., 190, pp. 515–526 (1989) "Copolymerization of Cycloalkenes with Ethylene In Presence of Chiral Zirconocene Catalysts" by W. Kaminsky and R. Spiehl.

Journal of Macromolecular Science: Reviews in Macromolecular Chemistry and Physics, C29(2&3), pp. 201–303 (1989) "A Review of High Resolution Liquid ^{13}Carbon

(List continued on next page.)

OTHER PUBLICATIONS

Nuclear Magnetic Resonance Characterizations of Ethylene-Based Polymers".

Journal of Non-Newtonian Fluid Mechanics, 36, pp. 255–263 (1990) "Additional Observations on The Surface Melt Fracture Behavior Of Linear Low-Density Polyethylene" by R. Moynihan, D. Baird, and R. Ramanathan.

Makromol. Chem. Rapid Commun., pp. 89–94 (1990) "Terpolymers of Ethylene, Propene and 1,5-Hexadiene Synthesized with Zirconocene/Methylaluminoxane" by W. Kaminsky and H. Drogemuller.

Journal of Rhelolgy, 35(4), 3 (May, 1991) pp. 497–552, "Wall Slip of Molten High Density Polyethylene. I. Sliding Plate Rheometer Studies" by S. G. Hatzikiriakos and J. M. Dealy.

Proceedings of the 1991 IEEE Power Engineering Society, pp. 184–190 (Sep. 22–27, 1991), "New Specialty Linear Polymers (SLP) For Power Cables" by Monica Hendewerk and Lawrence Spenadel.

Society of Plastic Engineers Proceedings, Polyolefins VII International Conference Feb. 24–27, 1991, "Structure/Property Relationships in Exxpol TM Polymers" (pp. 45–66) by C. Speed, B. Trudell, A. Mehta, and F. Stehling.

1991 Specialty Polyolefins Conference Proceedings, "The Marketing Challenge Created By Single Site Catalysts in Polyolefins," Sep. 24, 1991, (pp. 41–45) by Michael P. Jeffries.

High Polymers, vol. XX, "Crystalline Olefin Polymers" Part 1, pp. 495–501.

1991 Polymers, Laminations & Coatings Conference, TAPPI Proceedings, presented in Feb., 1991, pp. 289–296, "A New Family of Linear Ethylene Polymers with Enhanced Sealing Performance" by D. Van der Sanden and R. W. Halle.

Society of Plastic Engineers 1991 Specialty Polyolefins Conference Proceedings, pp. 41–55, "The Marketing Challenge Created by Single Site Catalysts in Polyolefins" by M. Jeffries (Sep. 24, 1991).

Advances In Polyolefins, by R. B. Seymour and T. Cheng, (1987), pp. 373–380 "Crystallinity and Morphology of Ethylene α-Olefin Copolymers" by P. Schouterden, G. Groeninckx, and H. Reynaers.

Advances In Polyolefins, by R. B. Seymour and T. Cheng (1987) "New Catalysis and Process For Ethylene Polymerization", pp. 337–354, by F. Karol, B. Wagner, I. Levine, G. Goeke and A. Noshay.

Advances In Polyolefins, by R. B. Seymour and T. Cheng, (1987) "Polymerization of Olefins With A Homogeneous Zirconium/Alumoxane Catalyst", pp. 361–371 by W. Kaminsky and H. Hahnsen.

ANTEC '92 Proceedings, pp. 154–158 ("Exact TM Linear Ethylene Polymers for Enhanced Sealing Performance" by D. Van der Sanden and R. W. Halle).

Society of Plastics Engineers, Polyolefins VII International Conference, Feb. 24–27, 1991, "Structure/Property Relationships in Exxpol TM Polymers", pp. 45–66, Speed et al.

ACS Symposium Series No. 142, "Polymer Characterization by ESR and NMR", by Randall Williams and Word in *Journal of Polymer Science, Polymer Letters*, vol. 6 p. 621 (1968).

Polymer Engineering and Science, vol. 17, No. 11, 1977, "Correlation of Low Density Polyethylene Rheological Measurements with Optical and Processing Properties", Shida et al.

Rheometers for Molten, John Dealy, Van Nostrand Reinhold Co. (1982), pp. 97–99.

The Encyclopedia of Chemical Technology, Kirtk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, vol. 16, pp. 415–417.

The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons New York, 1981, vol. 18, pp. 191–192.

Journal of Polymer Science, Poly. Phys. Ed., "Determination of Branching Distributions in Polyethylene and Ethylene Copolymers", vol. 20, pp. 441–455 (1982) Wild et al.

Journal of Rhelogy, "Wall Slip in Viscous Fluids and Influence of Materials of Construction", 30(2), pp. 337–257 (1986), by Ramamurthy.

Proceedings of the 1991 IEEE Power Engineering Society, pp. 184–190, Sep. 22–27, 1991, "New Speciality Linear Polymers (SLP) for Power Cables", by Hendewerk et al.

1992 Polymers, Laminations & Coatings Conference, pp. 103–111, "A New Family of Linear Ethylene Polymers with Enhanced Sealing Performance designed for Multilayer Barrier Food Packaging Films" by D. Van der Sanden and R. W. Halle.

1991 Polymers, Laminations & Coatings Conference, pp. 289–296, "A New Family of Linear Ethylene Polymers Provides Enhanced Sealing Performance" by Van der Sanden et al.

Feb. 1992 Tappai Journal, pp. 99–103, "A New Family of Linear Ethylene Polymers Provides Enhanced Sealing Performance" by Van der Sanden et al.

FIG. 1

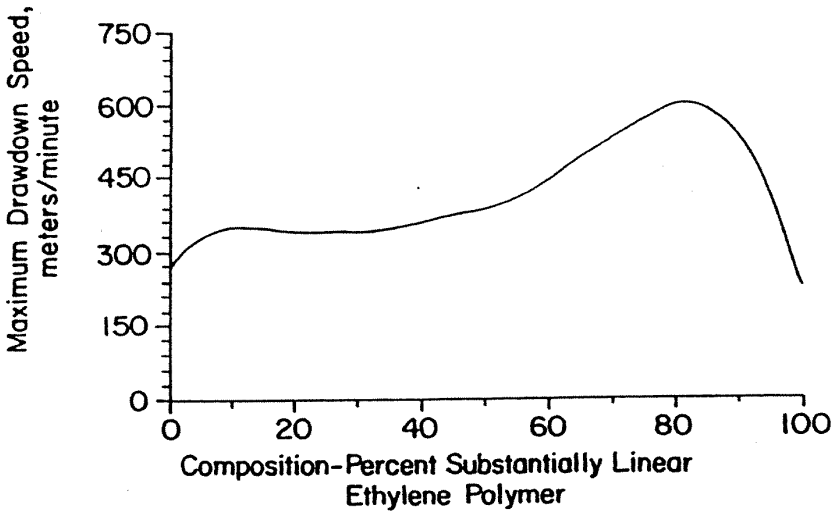
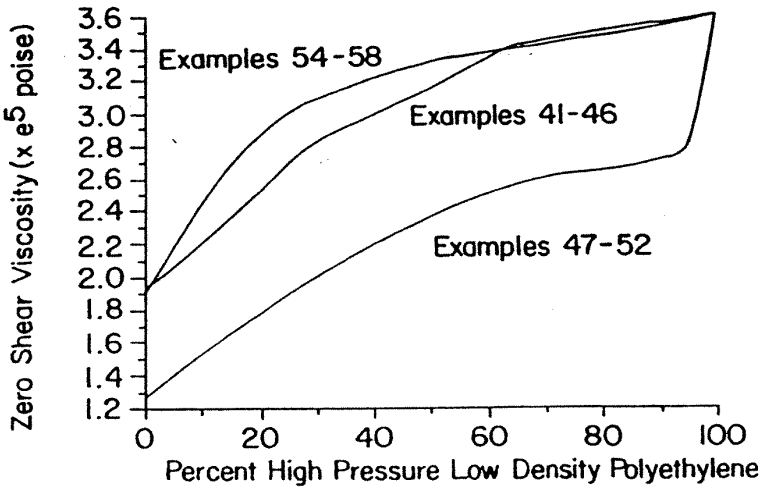

Maximum Drawdown Speed, meters/minute
750
600
450
300
150
0
0
20
40
60
80
100
Composition-Percent Substantially Linear Ethylene Polymer

FIG. 2


Zero Shear Viscosity (x e5 poise)
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
Examples 54-58
Examples 41-46
Examples 47-52
0
20
40
60
80
100
Percent High Pressure Low Density Polyethylene

HIGH DRAWDOWN EXTRUSION PROCESS WITH GREATER RESISTANCE TO DRAW RESONANCE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of pending application Ser. No. 07/776,130, filed Oct. 15, 1991, U.S. Pat. No. 5,272,236, in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson, James C. Stevens and Pak-Wing S. Chum, a continuation-in-part of pending application Ser. No. 07/939,281, filed Sep. 2, 1992, U.S. Pat. No. 5,278,272, in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens, a continuation-in-part of pending application Ser. No. 08/055,063, filed Apr. 28, 1993, in the names of Kim L. Walton, Rajen M. Patel, Pak-Wing S. Chum and Todd J. Obijeski and is related to pending application Ser. No. 07/961,269, filed Oct. 14, 1992, in the names of Kim Walton and Rajen Patel, the disclosures of all of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention pertains to an improved olefin extrusion composition, a process for extrusion coating a substrate or article, and a process for making an extrusion cast film. More particularly, this invention pertains to extrusion coating and extrusion cast film compositions with higher drawdown rates, lower neck-in and higher resistance to draw resonance. The extrusion compositions contain at least one substantially linear ethylene polymer as the thermoplastic component and may beneficially include at least one high-pressure ethylene polymer and/or at least one linear ethylene polymer.

2. Technical Background

It is known that low density polyethylene (LDPE) made by high-pressure polymerization of ethylene with free-radical initiators as well as heterogeneous linear low density polyethylene (LLDPE) and ultra low density polyethylene (ULDPE) made by the copolymerization of ethylene and α-olefins with Ziegler coordination (transition metal) catalysts at low to medium pressures can be used to extrusion coat substrates such as paper board as well as used to prepare extrusion cast film for applications such as disposable diapers and food packaging. However, although LDPE generally exhibits excellent extrusion processability and high extrusion drawdown rates, LDPE extrusion coatings and cast films lack sufficient abuse resistance and toughness for many applications. Conversely, while LLDPE and ULDPE extrusion coatings and cast films offer improved abuse resistance and toughness properties, these ethylene α-olefin polymers can not be extruded or drawn at high take-off rates and they are known to exhibit relatively poor extrusion processability.

The ultimate extrusion drawdown rate of known linear ethylene polymers is limited (at otherwise practicable extrusion line speeds) by the onset of a melt flow instability phenomena known as draw resonance rather than being limited by melt tension breaks due to "strain hardening" which occurs at higher line speeds and is typical for LDPE and other highly branched high pressure ethylene polymers such as, for example, ethylene-acrylic acid (EAA) copolymers and ethylene vinyl acetate (EVA) copolymers.

"Draw resonance" or "melt surging" occurs in LLDPE, ULDPE and other linear polymers such as high density polyethylene (HDPE), polypropylene and polyester during processing that involves rapid drawing or pulling of the melt such as extrusion coating, extrusion cast film fabrication, profile extrusion and fine denier fiber spinning. Also, the onset or occurrence of draw resonance is unmistakable.

The patent teachings of Kurtz et al. in U.S. Pat. No. 4,339,507 and Lucchesi et al. in U.S. Pat. No. 4,486,377 (the disclosures of both of which are incorporated herein by reference) describe draw resonance as a sustained random and/or periodic oscillation, variation or pulsation of the polymer melt with respect to the velocity and cross-sectional area of a melt drawing process that occurs between the die and the take-off position when the boundary conditions are a fixed velocity at the die and a fixed velocity at the take-off position. Draw resonance occurs when the draw ratio (i.e., the melt velocity at take-off divided by the melt velocity instantaneous at the die exit often approximated by dividing the reciprocal of the final polymer thickness by the reciprocal of the thickness of the melt instantaneous at the die exit) exceeds a polymer specific critical value. Draw resonance is a melt flow instability that is manifested as irregularities in the final coating, film or fiber dimensions and often produce widely variable thicknesses and widths. When line speeds significantly exceed the speed of onset, draw resonance can cause web or filament breaks and thereby shut down the entire drawing or converting process.

Given the various differences and intricacies that can exist between different extrusion equipment, relative resistance to draw resonance is often expressed in terms of critical draw ratio, and for conventional linear ethylene polymers, maximum stable draw ratios have been found to be less than 10:1, although draw ratios greater than 20:1 are needed for most commercial drawing operations.

"Drawdown" is defined herein to mean stretching or elongating a molten polymer extrudate (web or filament) in the machine direction and occasionally (simultaneously to a lesser degree) also in the transverse direction.

"Melt tension" which is also referred to in the relevant art as "melt strength" is defined and quantified herein to mean the stress or force (as applied by a wind-up drum equipped with a strain cell) required to draw a molten extrudate at some specified rate above its melting point as it passes through the die of a standard plastometer such as the one described in ASTM D1238-E. Melt tension values, which are reported herein in grams, are determined at 190 C. using a 2.16 kg weight and a 30 rpm wind-up rate. In general, for conventional linear and high pressure ethylene polymers, melt tension tends to increase with increased molecular weight, or with broadening of the molecular weight distribution and/or with increased melt flow ratios.

"Neck-in" which is influenced by extrudate swelling and, to lesser degree, by surface tension effects is defined herein as the difference between the die width and the web width at the taken-off position. Measured neck-in values (at constant output) will remain constant or decrease as the drawdown rate increases, and, in general, it is well known that for conventional ethylene polymers neck-in values increase as molecular weight decreases and/or as the molecular weight distribution narrows.

"Take-off position" is defined herein to mean the contact point (either the top or bottom) of a roller device that draws or pulls the molten extrudate down from its initial thickness instantaneous at the die exit to its final thickness. The roller device can be a nip roll, rubber roll, a chill roll, combinations thereof, or the like constructed from, for example, metal or rubber with various surfaces such as polished, matte or embossed finishes; all of which can to varying degrees affect the onset of draw resonance.

A variety of potential solutions have been disclosed to address the neck-in and/or draw resonance tendencies of linear polymers. Many of these solutions are equipment related and others primarily relate to modification of the properties of the linear polymers by forming polymer blends with highly branched high pressure ethylene polymers such as, for example, low density polyethylene. Thompson in U.S. Pat. No. 4,348,346 (which is incorporated herein by reference) is an example of equipment related attempts to address neck-in and draw resonance. Thompson describes a secondary injection of polymer melt streams into the primary die at the edges of the primary web stream is described to reduce neck-in and provide improved edge bead control.

An equipment modification solution specific to retarding the onset of draw resonance is provided by Cancio et al. in U.S. Pat. No. 4,668,463 and U.S. Pat. No. 4,626,574 (the disclosures of both of which are incorporated herein by reference) where locating a draw roller not more than 6 inches (15.2 cm) from the die provides a short air/draw gap and reduced draw resonance. Luchessi et al. in U.S. Pat. No. 4,486,377, teaches the use of a fluid medium, e.g., nitrogen, carbon monoxide or air, directed against the molten web prior to the take-off position as a viable method of retarding draw resonance. Similarly, Kurtz et al. in U.S. Pat. No. 4,608,221 (the disclosure of which is incorporated herein by reference) discloses that draw resonance can be mitigated by the utilization of a tensioning device with a friction free surface in a "rapid cooling zone" between the die and the take-off position.

Conversely, as another equipment modification example for alleviating or reducing draw resonance, Chaing in U.S. Pat. No. 4,859,379 (the disclosure of which is incorporated herein by reference) discloses radiant heating of the molten web prior to a chill roll take-off position.

Examples of modified linear polymer compositions exhibiting reduced draw resonance include U.S. Pat. No. 4,378,451 (Edwards), the disclosure of which is incorporated herein by reference, which discloses high flow rate compositions based on degraded propylene polymers blended with low density polyethylene. A similar example is provided by Werkman et al. in U.S. Pat. No. 3,247,290 (the disclosure of which is incorporated herein by reference) wherein thermally degraded (visbroken) high density polyethylene is blended with low density polyethylene to prepare high drawdown extrusion coating compositions. Another linear polymer blend example involving low density polyethylene is disclosed by Kurtz et al. in U.S. Pat. No. 4,339,507 where high pressure LDPE at 20 to 98 weight percent in combination with heterogeneous conventional LLDPE is taught to provide extrusion coating compositions with improved running rates.

An example of compositions that reduce draw resonance without the inclusion of a polymer degradation step and/or blending with a branched high pressure ethylene polymer is taught by Dohrer et al. in U.S. Pat. No. 4,780,264 where LLDPE with melt flow ratios less than 8.3 (i.e., utilizing molecular weight distributions even more narrow than typically employed) were found to allow surprisingly fast line speeds in extrusion coating and extrusion casting. However, predictably, these materials also exhibit higher neck-in and/or poor extrusion processability (e.g., higher extruder amperage).

In spite of the various advances, there is still a need for avoiding draw resonance and high neck-in problems when extruding known linear olefin polymer compositions at high extrusion line speeds. More particularly, there is also a need for extrusion coating and extrusion-casting materials that allow even higher line speeds and better extrusion processability than the lower melt flow ratio linear olefin polymers taught by Dohrer et al. in U.S. Pat. No. 4,780,264 and the polymer blends described by Kurtz et al. in U.S. Pat. No. 4,339,507. It is also desirable to avoid mechanical or equipment modifications that are designed to alter the drawing process itself as a means of attaining greater resistance draw resonance and lower neck-in. Additionally, to a lesser extent, there is also a desire to avoid the extra detail involved in providing appropriately degraded polymers as separately described by Werkman et al. and Edwards. As described hereinafter, the present invention substantially fills such desires and needs by providing compositions comprising at least one substantially linear ethylene polymer. However, if cast film or extrusion coating equipment modifications are already installed, and/or if blending with thermally degraded polymers is desired, or if the use of linear olefin polymers with lower melt flow ratios is desired, the present invention can still be employed to good advantage and the combined or synergistic benefits of the present invention and known solutions can also be realized.

SUMMARY OF THE INVENTION

In accordance with the present invention, we have discovered a new and improved:

Process for extrusion coating a substrate or for making a cast film with a thermoplastic composition, comprising the steps of:

(i) feeding a thermoplastic composition into at least one extruder,

(ii) melting and mixing the thermoplastic composition to form at least one uniform molten polymer stream,

(iii) extruding the molten polymer stream through a die to form a primary web,

the improvement comprising:

(i) operating said extruder at line speeds greater than 152 meters/minute, and either

(a) drawing down said web onto said substrate to thereby coat said substrate with at least one layer of said thermoplastic composition, or

(b) cooling and drawing down said web onto a take-off device to make said film with at least one layer of said thermoplastic composition,

(ii) conveying or collecting said coated substrate or said film for subsequent use, and

(iii) using as said thermoplastic composition:

(I) from about 10 to 100 percent by weight of at least one substantially linear ethylene polymer characterized as having:

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

(b) a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leqq (I_{10}/I_2)-4.63$,

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

(d) a single melting peak as determined using differential scanning calorimetry; and

(II) from 0 to about 90 percent by weight of at least one polymer selected from the group consisting of a heterogeneous linear ethylene polymer and high pressure ethylene polymer.

With the present invention, one obtains reduced neck-in, higher drawdown rates, and greater resistance to draw resonance than obtainable with heterogeneous linear ethylene polymers.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot showing the maximum drawdown rate as a function of weight percent of a 6.7 Melt Index substantially linear ethylene polymer blended with a 8 Melt Index high pressure low density polyethylene.

FIG. 2 is a plot of the zero shear melt viscosity as a function of weight percent high pressure low density polyethylene for two blends comprising substantially linear ethylene polymers with a high pressure low density polyethylene polymer and one blend comprising a conventional heterogeneous linear low density polyethylene polymer with a high pressure low density polyethylene polymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Substantially Linear Ethylene Polymers

The substantially linear ethylene polymers (either homopolymers or interpolymers) used in the present invention are a unique class of compounds that are further defined in copending application Ser. No. 07/776,130 filed Oct. 15, 1991 and in copending application Ser. No. 07/939,281 filed Sep. 2, 1992, each of which is incorporated herein by reference.

Substantially linear ethylene homopolymers and interpolymers are a truly unique class of ethylene polymers. They differ substantially from the class of conventional homogeneously branched linear ethylene/α-olefin copolymers described by Elston in U.S. Pat. No. 3,645,992, and moreover, they are not in the same class as conventional heterogeneous Ziegler polymerized linear ethylene polymers (e.g., ultra low density polyethylene, linear low density polyethylene or high density polyethylene made, for example, using the technique disclosed by Anderson et al. in U.S. Pat. No. 4,076,698, incorporated herein by reference, and utilized by Dohrer et al. as described in U.S. Pat. No. 4,780,264), nor are they in the same class as free-radical initiated highly branched high pressure low density ethylene homopolymer and ethylene interpolymers such as, for example, ethylene-acrylic acid (EAA) copolymers and ethylene-vinyl acetate (EVA) copolymers.

The substantially linear ethylene homopolymers and interpolymers useful in this invention have excellent processability, even though they have relatively narrow molecular weight distributions and exhibit improved resistance to draw resonance such that cast films and extrusion coatings with uniform dimensions can be prepared at higher extrusion line speeds. Surprisingly, in light of disclosures by Dohrer and Niemann (U.S. Pat. No. 4,780,264 and ANTEC Proceedings 1989, "Resistance to Draw Resonance of Linear Low Density Polyethylene Through Improved Resin Design", page 28–30), the melt flow ratio (I_{10}/I_2) of the substantially linear ethylene homopolymers or interpolymers can be varied widely and essentially independently of the polydispersity index (i.e., the molecular weight distribution, M_w/M_n). More particularly, this behavior is also a contradistinction to the linear ethylene/α-olefin copolymers described by Elston in U.S. Pat. No. 3,645,992 and to the heterogeneous conventional Ziegler polymerized linear polyethylene copolymers having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

The term "homogeneously branched" when applied to ethylene/α-olefin copolymers is defined herein to mean that (1) the α-olefin comonomer is randomly distributed within a given molecule, and (2) substantially all of the copolymer molecules have the same ethylene-to-comonomer ratio. When the term "homogeneously branched" is applied to both ethylene homopolymers and copolymers, it is defined herein to mean that (1) the polymer is characterized by a narrow short chain branching distribution where the short chain branching index (defined herein below) is greater than 30 percent, more preferably greater than 50 percent, and (2) the polymer essentially lacks a measurable high density (crystalline) polymer fraction as measured by known fractionation techniques such as, for example, a method that involves polymer fractional elutions as a function of temperature.

The term "high pressure" or "highly branched" is defined herein to mean that the polymer is partly or entirely homopolymerized or interpolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators.

The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like, where, at least one other comonomer is polymerized with ethylene to make the interpolymer.

The term "polymer" is used herein to indicate homopolymer and/or interpolymer, where ethylene is polymerized alone or with at least one other comonomer.

The term "thermoplastic" is used herein to indicate polymers or polymer compositions that are substantially thermally extrudable or deformable albeit relatively aggressive conditions may be required.

The term "substantially linear" means that the polymer backbone is substituted with about 0.01 long chain branch/1000 carbons to about 3 long chain branches/1000 carbons, more preferably from about 0.01 long chain branches/1000 carbons to about 1 long chain branch/1000 carbons, and especially from about 0.05 long chain branch/1000 carbons to about 1 long chain branch/1000 carbons.

The term "long chain branching" is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long chain branch can be about the same length as the length of the polymer back-bone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (*Rev.*

Macromol. Chem. Phys., C29, V. 2&3, p. 285–297), the disclosure of which is incorporated herein by reference.

The substantially linear homopolymers for use in the extrusion compositions, films, coatings and processes of the present invention are polymers of ethylene involving no additional monomer or comonomer although at least one chain transfer agent may be employed to affect specific polymer molecular characteristics. The substantially linear ethylene interpolymers for use in the present invention have a single melting peak, as opposed to conventional heterogeneous Ziegler polymerized polymers which have two or melting points as determined using differential scanning calorimetry (DSC). Also, the substantially linear ethylene polymers of the present invention are interpolymers of ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefin. Copolymers of ethylene and an α-olefin of C_3-C_{20} carbon atoms are especially preferred.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers, conjugated or non-conjugated dienes, polyenes, etc. Examples of such comonomers include C_3-C_{20} α-olefins as propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, and the like. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, e.g., cyclopentene, cyclohexene and cyclooctene.

The density of the substantially linear ethylene interpolymers or homopolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally greater than about 0.85 grams/cubic centimeter (g/cm^3), especially from about 0.86 g/cm^3 to about 0.96 g/cm^3, more preferably, from about 0.87 g/cm^3 to about 0.955 g/cm^3, and most preferably, from about 0.88 to about 0.95 g/cm^3.

The molecular weight of the substantially linear ethylene interpolymers or homopolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190 C./2.16 kilogram (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 melt index for the substantially linear ethylene interpolymers and homopolymers useful herein is generally from about 0.01 gram/10 minutes (g/10 min.) to about 40 g/10 min., preferably from about 0.1 g/10 min. to about 35 g/10 min., and especially from about 1 g/10 min. to about 20 g/10 min.

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

Unlike heterogeneous conventional linear polymers which possess no substantial long chain branching, for the substantially linear ethylene interpolymers and homopolymers used to prepare the extrusion compositions, cast films and extrusion coatings of the present invention, the melt flow ratio actually indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 melt flow ratio, the more long chain branching in the polymer. The I_{10}/I_2 ratio of the substantially linear ethylene interpolymers and homopolymers is preferably at least about 5.63, and especially from about 5.63 to about 18, and most especially from about 6 to about 15.

The "rheological processing index" (PI) which is defined herein as the apparent viscosity in kpoise of a polymer measured by a gas extrusion rheometer (GER), can also be used to distinguish the substantially linear ethylene polymers of this invention. The gas extrusion rheometer is described by M. Shida, R. N. Shroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, No. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97–99, both publications of which are incorporated by reference herein in their entirety. GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 250 to 5500 psig (17–379 bars) using about a 7.54 cm diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/cm^2. The unique substantially linear ethylene interpolymers and homopolymers described herein preferably have a PI in the range of about 0.01 kpoise to about 50 kpoise, preferably about 15 kpoise or less. The unique substantially linear ethylene interpolymers and homopolymers described herein have a PI less than or equal to about 70% of the PI of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S. Pat. No. 3,645,992) at about the same I_2 and M_w/M_n.

To more fully characterize the rheological behavior of the unique substantially linear ethylene polymers, S. Lai and G. W. Knight recently introduced (*ANTEC* '93 *Proceedings*, INSITE ™ Technology Polyolefins (ITP)—New Rules in the Structure/Rheology Relationship of Ethylene α-Olefin Copolymers, New Orleans, La., May 1993) another rheological measurement, the Dow Rheology Index (DRI), which expresses a polymer's "normalized relaxation time as the result of long chain branching." DRI ranges from 0 for polymers which do not have any measurable long chain branching (e.g., Tafmer ™ and Exact ™ products) to about 15 and is independent of melt index. In general, for low to medium pressure ethylene polymers (particularly at lower densities) DRI provides improved correlations to melt elasticity and high shear flowability relative to correlations of the same attempted with melt flow ratios, and for the substantially linear ethylene polymers of this invention, DRI is preferably at least about 0.1, and especially at least about 0.5, and most especially at least 0.8. DRI can be calculated from the equation:

$$DRI = (3652879 * \overset{*}{\tau_o}^{1.00649}/\eta_o - 1)/10$$

where τ_o is the characteristic relaxation time of the material and η_o is the zero shear viscosity of the material. Both τ_o and η_o are the "best fit" values to the Cross equation, i.e.

$$\eta/\eta_o = 1/(1+(\overset{\dagger}{\gamma} * \tau_o)^{1-n})$$

where n is the power law index of the material, and η and γ are the measured viscosity and shear rate, respectively. Baseline determination of viscosity and shear rate data are obtained using a Rheometric Mechanical Spectrometer (RMS-800) under dynamic sweep mode from 0.1 to 100 radians/second at 160 C. and a Gas Extrusion Rheometer (GER) at extrusion pressures from 1,000 psi to 5,000 psi (corresponding shear stress from 0.086 to 0.43 MPa) using a 7.54 centimeter diameter, 20:1 L/D die at 190 C. Specific material determinations can be performed from 140 to 190 C. as required to accommodate melt index variations.

For the substantially linear ethylene polymers of this invention, DRI relates linearly to draw ratio in accordance with the equation:

$$\text{Critical Draw Ratio} = 9.0641 + 29.264 * \text{DRI}$$

For the substantially linear ethylene polymers of the present invention, the molecular interrelationship between melt index, melt tension and maximum draw ratio before the onset of draw resonance is expressed by the following equation:

$$\text{Critical Draw Ratio} = a * MT - b * MI - c * MT^2 + d * MI^2 + e * MT * MI$$

where,

- a is a coefficient from about 39 to about 60, and especially from about 45 to about 53;
- b is a coefficient from about 7 to about 11, and especially from about 8 to about 10.5;
- c is a coefficient from about 33 to about 46, and especially from about 36 to about 43;
- d is a coefficient from about 0.5 to about 0.9, and especially from about 0.55 to about 0.85;
- e is a coefficient from about 13 to about 24, and especially from about 16 to about 21;
- MT is Melt Tension determined at 190 C. as described above; and
- MI is Melt Index determined in accordance with ASTM D1238 Condition 190 C./2.16 kg.

In addition to the onset of draw resonance and various rheological characterizations, ethylene polymers can also be distinguished by melt flow consequences that are manifested as solid state surface defects. Unlike draw resonance which is observed during drawing and pertains to irregularities in the extrudate dimension, an apparent shear stress versus apparent shear rate plot is used to identify the "melt fracture" phenomena which pertains to surface irregularities. According to Ramamurthy in the *Journal of Rheology*, 30(2), 337-357, 1986, above a certain critical shear rate (in contrast to a critical draw rate for the draw resonance phenomena), 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 film gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40× magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers and homopolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear homogeneously branched polymer as described by Elston in U.S. Pat. No. 3,645,992) having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady extrusion flow conditions, and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in cast films and bags therefrom), surface defects should be minimal, if not absent, for good film/coating quality and properties. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers and homopolymers used in the present invention is greater than about 4×10^6 dynes/cm^2. The critical shear rate at the onset of surface melt fracture (OSMF) and the 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.

The distribution of comonomer branches for the substantially linear ethylene interpolymers and homopolymers is characterized by its 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, by Wild et al., *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), or in U.S. Pat. No. 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the substantially linear interpolymers and homopolymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

The substantially linear ethylene interpolymers and homopolymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique. The substantially linear interpolymers and copolymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons. The "high density polymer fraction" can also be described as a polymer fraction with a degree of branching less than about 2 methyls/1000 carbons. Among other benefits, the lack of high density polymer fraction permits improved coating smoothness, printability, optical properties as well as enhanced film/coating flexibility and elasticity.

Molecular Weight Distribution Determination

The substantially linear ethylene interpolymers and homopolymers are analyzed by gel permeation chromatography (GPC) on a Waters 150 high temperature chromatographic unit equipped with differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of 10^3, 10^4, 10^5 and 10^6 Å. 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 milliliters/minute and the operating temperature is 140 C. with a 100-microliter injection size.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow mo-

lecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in *Journal of Polymer Science*, Polymer Letters, Vol. 6, p. 621, 1968, 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: $Mw = R w_i * M_i$, 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 the substantially linear ethylene interpolymers and homopolymers used in the present invention, the M_w/M_n is preferably from about 1.5 to about 8, and especially from about 1.7 to about 6.5.

Polymerization Catalysts for Substantially Linear Ethylene Polymers

Single site polymerization catalysts, (e.g., the monocyclo-pentadienyl transition metal olefin polymerization catalysts described by Canich in U.S. Pat. No. 5,026,798 or by Canich in U.S. Pat. No. 5,055,438, the disclosures of which are both incorporated herein by reference) or constrained geometry catalysts (e.g., as described by Stevens et al. in U.S. Pat. No. 5,064,802, incorporated herein by reference) can be used to polymerize the substantially linear interpolymers and copolymers, so long as the catalysts are used consistent with the methods described in U.S. Ser. No. 07/776,130 and in U.S. Ser. No. 07/939,281. Such polymerization methods are also described in PCT/U.S. Ser. No. 92/08812 (filed Oct. 15, 1992), the disclosure of which is incorporated herein by reference. However, the substantially linear ethylene interpolymers and homopolymers are preferably made by using suitable constrained geometry catalysts, especially constrained geometry catalysts as disclosed in U.S. application Ser. Nos.: 545,403, filed Jul. 3, 1990; 758,654, filed Sep. 12, 1991; 758,660, filed Sep. 12, 1991; and 720,041, filed Jun. 24, 1991, the teachings of all of which are incorporated herein by reference.

Suitable cocatalysts for use herein include but are not limited to, for example, polymeric or oligomeric aluminoxanes, especially methyl aluminoxane or modified methyl aluminoxane (made, e.g., as described in U.S. Pat. No. 5,041,584, U.S. Pat. No. 4,544,762, U.S. Pat. No. 5,015,749, and/or U.S. Pat. No. 5,041,585, the disclosures of each of which are incorporated herein by reference) as well as inert, compatible, non-coordinating, ion forming compounds. Preferred cocatalysts are inert, non-coordinating, boron compounds.

Preparation of the Substantially Linear Ethylene Polymer

The polymerization conditions for manufacturing the substantially linear ethylene homopolymers and interpolymers of the present invention are preferably those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Slurry and gas phase polymerization processes are also useful, provided the proper catalysts and polymerization conditions are employed. To polymerize the substantially linear interpolymers and copolymers useful in the invention, the single site and constrained geometry catalysts mentioned earlier can be used, but for substantially linear ethylene polymers the polymerization process should be operated such that the substantially linear polymers are formed. That is, not all polymerization conditions inherently make the substantially linear ethylene polymers, even when the same catalysts are used.

For example, in one embodiment of a polymerization process useful in making the novel substantially linear ethylene polymers, a continuous process is used, as opposed to a batch process.

Preferably, for substantially linear ethylene polymers, the polymerization is performed in a continuous solution polymerization process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively low for producing the substantially linear ethylene polymers using constrained geometry catalyst technology described herein is a function of reactor temperature and/or ethylene concentration. Reduced ethylene concentration and higher temperature generally produces higher I_{10}/I_2. Generally, as the ethylene concentration of the reactor decreases, the polymer concentration increases. For the novel substantially linear ethylene interpolymers and homopolymers, the polymer concentration for a continuous solution polymerization process is preferably above about 5 weight percent of the reactor contents, especially above about 6 weight percent of the reactor contents. Generally, the polymerization temperature of the continuous process, using constrained geometry catalyst technology, is from about 20 C. to about 250 C. If a narrow molecular weight distribution polymer (M_w/M_n of from about 1.5 to about 2.5) having a higher I_{10}/I_2 ratio (e.g. I_{10}/I_2 of about 7 or more, preferably at least about 8, especially at least about 9) is desired, the ethylene concentration in the reactor is preferably not more than about 8 percent by weight of the reactor contents, especially not more than about 6 percent by weight of the reactor contents, and most especially not more than about 4 percent by weight of the reactor contents.

Multiple reactor polymerization processes can also be used in making the substantially linear olefin interpolymers and homopolymers of the present invention, such as those processes disclosed in copending applications Ser. No. 07/815,716 filed Dec. 30, 1991 and Ser. No. 08/010,958 filed Jan. 29, 1993, and in U.S. Pat. No. 3,914,342, the disclosures of all of which are incorporated herein by reference. The multiple reactors can be operated in series or in parallel or a combination thereof, with at least one constrained geometry catalyst employed in at least one of the reactors.

Additional Embodiments

Additives such as antioxidants (e.g., hindered phenolics such as Irganox ®1010 or Irganox ®1076 supplied by Ciba Geigy), phosphites (e.g., Irgafos ®168 also supplied by Ciba Geigy), cling additives (e.g., PIB), Standostab PEPQ ™ (supplied by Sandoz), pigments, colorants, fillers, and the like can also be included in the interpolymers and copolymers of the present invention, to the extent that they do not interfere with the improved draw resonance resistance discovered by Applicants. The extrusion coatings and films may also contain additives to enhance antiblocking and coefficient of friction characteristics including, but not limited to,

untreated and treated silicon dioxide, talc, calcium carbonate, and clay, as well as primary, secondary and substituted fatty acid amides, chill roll release agents, silicone coatings, etc. Other additives may also be added to enhance the anti-fogging characteristics of, for example, transparent cast films, as described, for example, by Niemann in U.S. Pat. No. 4,486,552, the disclosure of which is incorporated herein by reference. Still other additives, such as quaternary ammonium compounds alone or in combination with ethylene-acrylic acid (EAA) copolymers or other functional polymers, may also be added to enhance the antistatic characteristics of coatings and films of this invention and allow, for example, the packaging of electronically sensitive goods.

The substantially linear ethylene polymers used to prepare the compositions and products of the present invention can be blended with linear ethylene polymers and/or high pressure ethylene polymers, or used as the only resinous polymer component whether the resultant film or coating to be used is a monolayer or multilayer construction. Still other polymers can also be blended with the substantially linear ethylene interpolymers or homopolymers to modify processing, film strength, heat seal, or adhesion characteristics.

Some useful materials for blending with substantially linear ethylene interpolymers and homopolymers include, for example, but are not limited to, low density ethylene polymer such as high pressure low density ethylene homopolymer (LDPE), ethylene-vinyl acetate copolymer (EVA), ethylene-carboxylic acid copolymers and ethylene acrylate copolymers as well as olefin polymers produced at low to medium pressures such as polybutylene (PB) and ethylene/α-olefin polymers which includes high density polyethylene, medium density polyethylene, polypropylene, ethylene-propylene interpolymers, linear low density polyethylene (LLDPE) and ultra low density polyethylene, as well as graft-modified polymers, and combinations thereof including I_{10}/I_2, MWD, and/or comonomer combinations.

Suitable high pressure ethylene interpolymers include ethylene interpolymerized with at least one α,β-ethylenically unsaturated comonomers (e.g., acrylic acid, methacrylic acid and vinyl acetate) as described by McKinney et al. in U.S. Pat. No. 4,599,392, the disclosure of which is incorporated herein by reference. Preferred high pressure ethylene interpolymers comprise from about 0.1 to about 55 total weight percent comonomer, and more preferably from about 1 to about 35 total weight percent comonomer, and most preferably from about 2 to about 28 total weight percent comonomer, and can be chemically and/or physically modified by any known technique such as, for example, by ionomerization and extrusion grafting.

However, preferred polymer blends comprise at least one substantially linear ethylene polymer, and preferably the substantially linear ethylene interpolymer or homopolymer comprises at least about 5 percent of the blend composition, more preferably at least about 10 percent of the blend composition.

For the multilayer coatings and films of the present invention, any layer and any number of layers can comprise at least one substantially linear ethylene polymer. However, highly preferably, though, for multilayer film and coating constructions, outer layers (alternatively referred to in the art as "skin layers" or "surface layers") and sealant layers would comprise at least one substantially linear ethylene interpolymer and/or homopolymer.

The blend compositions of this invention can be prepared by any suitable means known in the art including tumble dry-blending, melt blending via compound or side-arm extrusion, or the like as well as combinations thereof. Also, the multilayer constructions of this invention can be prepared by any means known including coextrusion, laminations and the like and combinations thereof. Moreover, compositions of this invention can be employed in coextrusion operations where a higher drawdown material is used to essentially "carry" one or more lower drawdown materials. The blended and non-blended compositions of this invention, whether of monolayer or multilayer construction, can be used to coat various polar and nonpolar substrates including for example, but not limited to, paper products, metals, ceramics, glass and various polymers, particularly other polyolefins, and combinations thereof.

EXAMPLES

The following examples illustrate some of the particular embodiments of the present invention, but the following should not be construed to mean the invention is limited to the particular embodiments shown. Also, practitioners of these arts will appreciate that the maximum line speeds attainable with one type of extruder or coater will not necessarily be the same as the speeds attainable with another and the same equipment arrangement should be used for meaningful comparisons.

Examples 1–6

In the following Examples 1–6, Table 1 summarizes the polymers used in an extrusion coating evaluation. The coating equipment consists of a two-extruder Black Clawson coextrusion coating line with a 3½ inch (8.9 cm) diameter primary extruder with a 30:1 L/D and a 2½ inch (6.4 cm) diameter secondary extruder with a 24:1 L/D. A 76 cm slot die is attached and deckled to 69 cm with a 20 mil die gap and a 6 inch (15.2 cm) air/draw gap. The targeted extrusion temperature and screw speed for all extrusion coating examples is 610 F. (316 C.) and 90 rpm, respectively, unless otherwise noted. Molten webs are drawn down to continuous 50 lb. Kraft paper as well as to slip-sheets of aluminum and oriented polypropylene.

TABLE 1

Sample	Polymer Type	Melt Index (g/10 min.)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	M_w/M_n
A	SLEP	4.5	0.902	7.4	2.15
B	SLEP	4.7	0.910	8.0	2.28
C	SLEP	9.4	0.910	7.5	2.28
D	SLEP	8.1	0.913	6.7	ND
E*	LINEAR	4.0	0.904	7.9	ND
F*	LINEAR	5.4	0.911	7.6	3.4

*Not an example of the present invention; provided for comparative purposes only.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LINEAR = heterogeneous conventional ultra low density polyethylene prepared by the interpolymerization of ethylene and 1-octene as described in U.S. Pat. No. 4,076,698 and 4,780,264.
ND = not determined.

Samples A–F are evaluated on the above described Black Clawson coextrusion line. The evaluation involved systematically increasing the take-off speed while maintaining a constant screw speed (90 rpm). The line speed where the onset of draw resonance (i.e., web began to oscillate) is initially observed, is taken as the ultimate or maximum drawdown rate. The drawdown

rate, neck-in measured at a 440 fpm (134 mpm) line speed for a 1 mil coating thickness and the output rate at ultimate drawdown are summarized in Table 2 for these samples.

TABLE 2

Example	Sample	Extrusion Coating Results on Draw Resonance and Neck-In: Drawdown † Rate ft/min. (mpm)	Neck-In at 134 mpm/1 Mil (cm)	Output (kg/hr/hp)
1	A	600 (183)	21	3.2
2	B	650 (198)	21	3.4
3	C	780 (238)	21	3.9
4	D	570 (174)	24	3.2
5*	E	350 (107)	**	2.9
6*	F	440 (134)	23	ND

Drawdown rate = take-off speed at which dimensional irregularities are observed to initially occur.
*Not an example of the present invention; provided for comparative purposes.
**Draw resonance onset at 107 mpm, could not achieve 134 mpm to produce a uniform 1 mil coating and obtain comparative neck-in measurements.
ND = not determined.

As can be observed from the data in Table 2, relative to heterogeneous conventional linear ethylene polymers, extrusion coating compositions comprising substantially linear ethylene polymers allow greater resistance to draw resonance whereby higher extrusion line speeds are attainable. Surprisingly, in contradistinction to Dohrer et al. in U.S. Pat. No. 4,780,264 and to the blends described by Kurtz et al. in U.S. Pat. No. 4,608,221, the substantially linear polymers show higher comparative drawdown rates even at higher melt flow ratios. Table 1 also shows that substantially linear polymers exhibit less neck-in than heterogeneous conventional linear polymers, even at appreciably higher melt indices, and these unique polymers also provide higher extruder pumping rates (as measured as higher specific outputs) which is indicative of more efficient, improved processability.

Samples G–K

Table 3 shows the polymers used (Sample G–K) for an extrusion cast embossed evaluation where the extrusion equipment consists of a three-extruder cast coextrusion film line with a 20/60/20 feedblock design and a slot die. The extruder diameters are 2½, 3½ and 2 inches (6.4, 8.9 and 5.1 cm), respectively, and the die width measures 76 cm with a 20-mil manual die gap. The evaluation involves a primary chill roll with either a chrome polished finish (4–5 rms. surface roughness) or a matte finish (32 rms. surface roughness), and a secondary chill roll with a chrome polished finish (4–5 rms. surface roughness). The line is also equipped with a beta thickness gauge, a nip roll with a silicon-based rubber cover, a squeegee roll and a recirculating water trough system. Table 4 shows the extrusion cast line conditions that are held constant for these polymer evaluations.

TABLE 3

Sample	Polymer Type	Polymer Descriptions for Extrusion Casting Evaluation: Melt Index (g/10 min.)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	Melt Tension (grams)
G	SLEP	2.5	0.935	8.8	1.04
H	SLEP	2.4	0.934	11.4	1.46
I*	LINEAR	2.4	0.934	7.4	0.65
J*	LINEAR	4.0	0.941	6.7	0.41
K*	LDPE	2.0	0.922	10.5	3.8

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LINEAR = heterogeneous conventional linear low density polyethylene prepared by the interpolymerization of ethylene and 1-octene as described in U.S. Pat. No. 4,076,698 and U.S. Pat. No. 4,780,264.
LDPE = traditional high pressure low density polyethylene.

TABLE 4

Constant Conditions for Extrusion Casting Evaluation	
Melt Temperature, C.	274
Nip Roll Height, cm	29
Draw Gap, cm	18
Final Film Thickness, mils	1
Chill Roll Temperature, C.	21–27
Nip Roll Temperature, C.	27
Water Bath Temperature, C.	27–35

The onset of extrusion casting draw resonance as defined as maximum drawdown rate is determined by incrementally increasing the line speed (take-off rate) while concurrently increasing the screw speed to maintain a constant film thickness at 1 mil until definitive dimension fluctuations are observed for each polymer. The onset of extrusion cast draw resonance is also indicated by minimum uniform film thickness or maximum downgaugability. Maximum downgaugability is determined by increasing line speed at a constant extrusion output rate for each polymer. Neck-in is determined by measuring the difference between the die width and the width of the web at the primary chill roll. Table 5 illustrates the evaluation results for the onset of draw resonance by both maximum drawdown rate and downgaugability as well as the extrusion output at maximum drawdown for each polymer evaluated. Table 5 also includes results for Inventive Example 12 which is 70/30 weight percent blend of comparative sample J and Inventive Sample H, respectively.

TABLE 5

Example	Sample	Extrusion Casting Evaluation: Maximum Drawdown Rate (meters/min.)	Maximum Downgaugability † (mils)	Neck-In 91 mpm/1 Mil (cm)	Output at Max Drawdown (kg/hr)
7	G	174	0.82	23	200
8	H	>300	<0.76	20	>315
9*	I	53	1.83	ND	<68
10*	J	127	1.06	27	113
11*	K	>300	ND	ND	ND
12[a]	L	>152	ND	ND	ND

*Not an example of the present invention, provided for comparative purposes only.
Total extruder output constant at approximately 138 kg/hr.
ND = not determined.
[a]Ample quantities were not available to fully determine maximum drawdown rate and neck-in.

Table 5 shows that the unique substantially linear ethylene polymers of this invention allow significant advantages and/or improvements in drawdown rates,

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downgaugability, neck-in and output in comparison to heterogeneous conventional linear ethylene polymers. Also, contrary to the disclosure by Dohrer et al. (U.S. Pat. No. 4,780,264), the substantially linear ethylene polymer sample (Sample H) with the highest melt flow ratio and highest melt tension exhibits line speeds comparable to low density polyethylene.

Examples 7–12: Film Properties

Table 6 shows that extrusion casting compositions comprising a substantially linear ethylene polymer allow a superior balance of cast film abuse properties and toughness over low density polyethylene at 1.0 mil film thickness. With few exceptions, Table 6 indicates compositions involving a substantially linear ethylene polymer generally provide at least 30 percent better abuse resistance properties (i.e., yield strength, toughness, tear resistance and dart impact resistance) relative to comparative low density polyethylene cast film. Given the higher density of the substantially linear ethylene polymer compositions (0.934 g/cm^3 versus 0.922 g/cm^3 for the comparative LDPE sample), the superior abuse resistance and toughness properties are surprising. Ethylene polymers typically show improved mechanical and abuse resistance properties at lower densities. This relationship is especially true for ethylene/α-olefin copolymers where higher comonomer levels provide lower densities and superior toughness. In general, higher density ethylene polymers, and more particularly, medium density (i.e., 0.93 g/cm^3–0.945 g/cm^3) polymers with 1 percent secant moduli above 30,000 psi (207 MPa), are required in cast embossed applications that demand improved convertibility or machineability, i.e., the ability for the film to move and/or be handled smoothly as it passes from one converting or constructing operation to the next until the final desired product is produced.

TABLE 6

Extrusion Cast Film Property Comparisons

Example	Sample	Line Speed for 1 mil film (m/min.)	Yield Strength † (MD + TD)/2 (MPa)	Toughness † (MD + TD)/2 MJ/m^3	TD Tear †† Resistance (grams)	Dart Impact ††† (grams)
7	G	91	11.2	84.4	118	55
8	H	152	10.8	62.5	198	38
9*	I	30	9.8	85.6	206	66
10*	J	91	12.7	92.2	92	45
11*	K (LDPE)	152	7.8	60.0	124	34
12	L	152	11.8	78.6	181	45

*Not an example of the present invention; provided for comparative purposes only.

Constant extrusion conditions: 18 cm draw gap, 274 C. melt temperature for all three extruders, 3.4 bars nip pressure, 27 C. nip roll temperature, 21–27 C. chill roll temperature, and 27–35 C. water bath temp.

Tensile yield strength and toughness are determined in accordance with ASTM D882 where toughness is taken as the integration of the area under the stress/strain curve.

Elmendorf tear resistance is determined in accordance with ASTM D1922; only transverse direction (TD) resistance is reported since it's most important for cast film applications such as disposable diapers as described by Roberts et al. in ANTEC Proceedings '85, pp. 104–7 and by Lucchesi et al., in Plastics Engineering, May 1985, pp. 87–90, the disclosures of both of which are incorporated herein by reference.

Dart impact is determined in accordance with ASTM D1709 Method A.

Examples 7–9: Extrusion Processability

Another evaluation is conducted to further quantify the superior processability of the unique compositions of the present invention. Inventive samples G and H and comparative sample I, all with similar melt indices and polymer densities, were extrusion casted at a constant output rate (i.e., approximately 138 kg/hour). The corresponding amperages and extrusion pressures for each extruder are listed in Table 7.

TABLE 7

Extrusion Casting Processibility Evaluation

Example	7 Inventive Sample G	8 Inventive Sample H	9 Comparative* Sample I
Screw Speed (rpm)			
6.4 cm Extruder	15.2	16.5	15.6
8.9 cm Extruder	44.7	49.5	45.6
5.1 cm Extruder	33.4	36.8	34.2
Extruder Amperage			
6.4 cm Extruder	16	14	21
8.9 cm Extruder	87	68	108
5.1 cm Extruder	12	11	15
Extruder Pressure (MPa)			
6.4 cm Extruder	11.4	9.0	15.0
8.9 cm Extruder	14.1	10.8	17.9
5.1 cm Extruder	9.2	7.5	12.8

*Not an example of the present invention; provided for comparative purposes only. Constant extrusion conditions: 18 cm air/draw gap, 274 C. melt temperature for all three extruders, 3.4 bars nip pressure, 27 C. nip roll temperature, 21–27 C. chill roll temperature., and 27–35 C. water bath temperature.

As Table 7 shows, compositions of this invention exhibit the significantly lower amperages and extrusion pressures which is indicative of more efficient processibility, i.e., lower energy consumption for the same output.

Examples 13–20

In another evaluation, Inventive Samples A, B and C, as well as two other substantially linear ethylene polymers (Inventive Samples M and N) are tumble dry-blended at a 82/18 ratio with a traditional high pressure low density polyethylene to prepare extrusion coating compositions. The compositions are evaluated for the onset of draw resonance on the Black Clawson extrusion coater described above. The Black Clawson coater is operated substantially as indicated above in Example 1 and Table 8 shows the polymer descriptions for Inventive Sample M and N as well as for the LDPE blend component material. Table 9 shows resultant melt index, drawdown, neck-in and output performance for these various extrusion compositions as well as two additional inventive compositions involving two high pressure ethylene copolymers, i.e., an ethylene-acrylic acid (EAA) copolymer and an ethylene-methyl acrylate (EMA) copolymer. Like the coating operation, the drawdown, neck-in and output determinations are performed substantially as indicated for Examples 1–6.

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TABLE 8

Sample	Polymer Type	Melt Index (g/10 min.)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	M_w/M_n
M	SLEP	6.7	0.903	7.4	2.12
N	SLEP	28.0	0.898	6.3	2.23
O*	LDPE	7.9	0.916	ND	7.85
P*	LDPE	4.2	0.923	ND	ND

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LDPE = traditional high pressure low density polyethylene.
ND = not determined.

TABLE 9

Example	Base Polymer (Sample #)	High Pressure Ethylene Polymer (18% by wt.)	Melt Index (g/10 min)	Maximum Drawdown (m/min.)	Neck-In 134 mpm/1 Mil (cm)	Output (kg/hr/hp)
		Extrusion Coating Blend Compositions				
1	A	None	4.5	183	21	3.2
13	A	LDPE	ND	549	9.9	3.5
14	A	EMA	ND	305	18.5	3.4
15	A	EAA	ND	219	17.3	3.5
16	B	LDPE	4.7	>610	9.9	3.8
17	C	LDPE	8.5	>610	9.9	4.4
18	M	LDPE	6.4	>610	12.7	3.7
19[a]	N	LDPE	ND	564	10.2	4.2
20*	F	LDPE	5.4	524	14.2	3.5

*Not an example of the present invention; provided for comparative purposes only.
[a]The blend combination of Sample N and sample O (Inventive Example 19) is extruded at a reduced extrusion melt temperature (270 C.) due the high melt index of Inventive Sample N.
EMA = ethylene methyl acrylate copolymer comprised of 20 wt. % methyl acrylate and having a 6 MI.
EAA = ethylene acrylic acid copolymer, supplied by The Dow Chemical Company as PRIMACOR TM 4608, comprised of 6.5 wt. % acrylic acid and having an 8 MI.
LDPE = Sample O.
ND = not determined.

Table 9 shows blending minor amounts of a highly branched ethylene polymer into a substantially linear ethylene polymer provides extrusion compositions with excellent drawdown performance, lower neck-in and improved specific output. Table 9 also show compositions comprised of the substantially linear ethylene polymers of this invention are superior to comparative linear ethylene polymer compositions, particularly with respect to neck-in at higher drawdown rates. The ability to achieve less neck-in at a higher drawdown rate, not only allows maximum downgaugability, it also provides practitioners the advantage and flexibility to lower the melt index to gain additional strength property improvements.

Example 21–27

In another extrusion coating evaluation, blends are prepared using Inventive Sample M and comparative LDPE sample K as well as another highly branched high pressure LDPE sample (comparative sample P). Descriptions for Inventive Sample M and the LDPE sample P are listed in Table 8. Using these polymers, extrusion coating compositions are prepared dry-blending as described above in Examples 13–20 unless noted otherwise. The compositions are evaluated on the Black Clawson extrusion coater (described above) by increasing the take-off rate at constant screw speed (90 rpms) and deducing the onset of draw resonance. As another part of the evaluation, while being drawn at a constant 440 ft/min. (134 meter/min.), sheets of 0.5 mil oriented polypropylene (OPP) film are slip-sheeted at the die to prepare extrusion laminates for adhesion testing. Table 10 shows the blend composition sample descriptions and extrusion melt temperatures as well as the drawdown, neck-in and OPP adhesion performance for the various compositions evaluated. Inventive Samples 23–27 employ Inventive Sample M.

TABLE 10

Example	Weight % LDPE (Sample O)	Melt Temperature (C.)	Maximum Drawdown (m/min.)	Neck-In at 134 mpm/1 Mil (cm)	OPP Adhesion (g/cm)
		Additional Extrusion Coating Blend Compositions †			
21*	100	330	268[a]	4.1	14.3
22*	100	332	271[a]	5.1	5.4
23	90	329	357	4.8	23.2
24	90	328	366	5.8	7.1
25	70	317	344	5.1	46.4
26	50	318	390	6.4	250
27	18	314	>610	12.7	>286

Black Clawson coextrusion coater line is operated at a screw speed of 90 rpm for ~113 kg/hr.
*Not an example of the present invention; provided for comparative purposes only.
[a]Draw resonance was not observed; maximum drawdown deduced by melt tension breakage manifested as edge tears.
LDPE = Sample P instead of Sample O.

FIG. 1 is a plot showing the maximum drawdown rate as a function of weight percent of a 6.7 Melt Index substantially linear ethylene polymer blended into a 8 Melt Index high pressure low density polyethylene where the blends comprise extrusion compositions. Surprisingly, FIG. 1 together with Table 10 illustrate that these extrusion compositions show synergistic drawdown performance, i.e., the drawdown rates of the combinations are higher than that of either polymer used alone. The synergistic performance and the discovery that the optimum or maximum drawdown performance occurs for compositions comprised of less than about 20 weight percent LDPE into at least one substantially linear polymer, is a contradistinction over the art provided by Kurtz et al. in U.S. Pat. No.

4,339,507 where LDPE blend combinations with a heterogeneous conventional linear ethylene polymer provide synergistic drawdown performance only when the composition is comprised of "greater than 20 weight percent and less than 98 weight percent of a high pressure LDPE" and, according to FIG. 4 provided by Kurtz et al. in U.S. Pat. No. 4,339,507, the optimum amount of LDPE is about 45–50 weight percent for maximum synergistic drawdown performance. Moreover, on a percentage basis (which takes account of extrusion equipment differences), the apparent optimum illustrated in FIG. 1 of this invention represents a more significant drawdown improvement or increase relative to the disclosed discoveries of Kurtz et al. Further, Table 10 also shows that the present inventive compositions provide exceptional and/or synergistic OPP adhesion when extrusion laminated or the like.

Examples 28–39: Ternary Polymer Blends

In the same manner as described for Examples 21–27, ternary blends are prepared using a substantially linear ethylene polymer, a linear ethylene polymer and a high pressure low density polyethylene polymer. The various blend combinations of these polymers is reported in Table 11. As dry-blended extrusion coating compositions, the polymer blends are evaluated on the Black Clawson extrusion as described in Example 5 to determine drawdown and neck-in performance. Resultant paper coatings and uncoated Kraft paper are also evaluated for tear resistance using the Elmendorf Tear method in accordance with ASTM D1938. The neck-in, drawdown rate before the onset of draw resonance and tear properties as well as polymer descriptions are all reported in Table 11.

TABLE 11

	Ternary Polymer Blends					
Example	LDPE (wt. %)	ULDPE (wt. %)	SLEP (wt. %)	Neck-In 134 mpm/1 Mil (cm)	Maximum Drawdown (m/min.)	Tear Resistance (grams) †
28*	100	0	0	5.5	305	121
29*	20	80	0	10.9	>610	275
30*	80	20	0	4.8	380	134
31	80	0	20	4.8	450	134
32	20	0	80	10.9	>610	290
33	20	70	10	11.4	>610	253
34	20	50	30	11.7	>610	287
35	20	30	50	11.4	>610	276
36	70	20	10	5.3	405	155
37	50	20	30	6.1	415	298
38	30	20	50	8.4	>610	252
39[b]	0	0	0	NA	NA	92

*Not an example of the present invention; used for comparative purposes only.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene having a 8.1 Melt Index and a 0.913 g/cc density.
LDPE = traditional high pressure low density polyethylene; Comparative Sample O.
ULDPE = heterogeneous conventional ultra low linear low density olefin polymer of ethylene and 1-octene having a 6.0 Melt Index and a 0.911 g/cc density.
NA = not applicable.
† Tear resistance values are reported as (machine direction + transverse direction)/2.
[b]Sample 39 is uncoated Kraft paper and is not an example of the present invention.

Table 11 shows that the ternary combination of substantially linear ethylene polymers with high pressure polyethylene and linear ethylene polymers can allow improved drawdown rates and improved tear properties in comparison to high pressure polyethylene used alone in an extrusion coating operation. Also, Table 11 shows that ternary blend compositions based on substantially linear ethylene polymers offer better overall performance attributes with respect to neck-in, drawdown and tear properties when compared to known blend combinations involving high pressure polyethylene and heterogeneous conventional linear ethylene polymers.

FIG. 2: Melt Elasticity

In another experiment, the relative melt tension or melt elasticity of inventive blends and heterogeneous conventional blend compositions is determined. The experiment involved two substantially linear ethylene polymers, one heterogeneous linear low density polyethylene and one high pressure low density polyethylene. The property descriptions of these raw materials are listed in Table 12. Melt blends of the substantially linear ethylene polymers with LDPE and a blend of LLDPE with LDPE were prepared by melt mixing the components in a Haake Rheocorder mixer at a 160 C. melt temperature and 40–60 rpm rotor speed for a total of five minutes. The resultant blends are granulated and compression molded into 3 mm thick plates for melt elasticity testing. The pure components (base polymers) are also subjected to identical Haake mixer treatment. The melt index (I_2) and melt tension are determined for the resultant blends and pure components as described above. The melt elasticity is determined by using a Rheometrics Dynamic Analyzer II where the dynamic shear viscosity experiment is performed from 0.05 Hz to 100 Hz under 15% strain at 160 C. and the melt viscosity at zero shear rate is interpolated from the resultant plot. Table 13 shows the melt index, melt tension and zero shear viscosity for the three polymer blends. FIG. 2 is a plot of zero shear melt viscosity as a function of weight percent high pressure low density polyethylene in the blend. These data show that polymer blends involving a substantially linear ethylene homopolymer and copolymer exhibit synergistic melt elasticity behavior (opposed to linear or directly additive behavior) as measured by zero shear viscosity which represents the unperturbed chain entanglement capability. Higher zero shear viscosity and chain entanglement capability, which is the origin of melt strength, is thought to relate directly with long chain branching and allows for the build up of melt stress during high shear drawing at high line speeds.

TABLE 12

Polymer Blend Raw Materials

Sample	Polymer Type	Melt Index, I_2 (g/10 min)	Density (g/cc)	Melt Tension (grams)	I_{10}/I_2
Q	SLEP	1.03	0.9192	1.9	9.4
R	SLEP†	0.97	0.9512	3.0	12.1
S*	LINEAR	1.0	0.920	1.2	8.0
T*	LDPE	0.7	0.923	9.8	9.8

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene with 1-octene.
SLEP = substantially linear ethylene polymer prepared by the homopolymerization of ethylene.
LDPE = traditional high pressure low density polyethylene.
LINEAR = heterogeneously linear low density polyethylene prepared by the interpolymerization of ethylene with 1-octene; supplied by The Dow Chemical Company under the trademark of DOWLEX TM 2045.
ND = not determined.

TABLE 13

Melt Elasticity of Haake-Mixed Polymer Blends

Example	Base Polymer (Sample #)	% LDPE (Sample T)	Melt Index (g/10 min.)	Melt Tension (grams)	Zero Shear Viscosity (X e^5 poise)
40*	T	100	14.08	12.63	3.6
41	Q	80	13.08	11.56	3.5
42	Q	65	12.19	11.45	3.41
43	Q	50	10.54	10.93	3.15
44	Q	30	3.89	10.24	2.83
45	Q	10	2.36	9.71	2.2
46	Q	0	3.65	9.21	1.93
47*	T	100	ND	ND	3.6
48*	S	95	ND	ND	2.76
49*	S	85	ND	ND	2.66
50*	S	70	ND	ND	2.6
51*	S	30	ND	ND	1.99
52*	S	0	ND	ND	1.26
53*	T	100	13.79	11.8	3.6
54	R	90	16.96	13.34	3.52
55	R	80	14.65	13.33	3.47
56	R	50	11.11	13.13	3.31
57	R	20	6.74	14.13	2.87
58	R	0	3.01	13.01	1.9

*Not an example of the present invention; provided for comparative purposes.
ND = not determined.

Examples 59–65: Molecular Interrelationships

In another extrusion coating evaluation, draw ratio is approximated from web thicknesses. The molecular interrelationship between melt index, melt tension and maximum draw ratio before the onset of draw resonance is elucidated by performing standard least squares regression analysis on the dataset shown in Table 14. The following equation shows the interrelationship:

$$\text{Critical Draw Ratio} = a * MT - b * MI - c * MT^2 + d * MI^2 + e * MT * MI$$

where,

a is a coefficient from about 39 to about 60, and especially from about 45 to about 53;

b is a coefficient from about 7 to about 11, and especially from about 8 to about 10.5;

c is a coefficient from about 33 to about 46, and especially from about 36 to about 43;

d is a coefficient from about 0.5 to about 0.9, and especially from about 0.55 to about 0.85;

e is a coefficient from about 13 to about 24, and especially from about 16 to about 21;

MT is Melt Tension determined at 190 C. as described above; and

MI is Melt Index determined in accordance with ASTM D1238 Condition 190 C./2.16 kg.

TABLE 14

Molecular Interrelationships

Example	Blend Component(s)	Component Weight %	Melt Index (g/10 min)	Melt Tension (grams)	Draw Ratio
59	Sample A	100	4.5	0.46	28
60	Sample B	100	4.7	0.53	31
61	Sample C	100	9.4	0.28	35
62*	Sample O	100	7.9	4.48	49
63	Sample A/O	90/10	4.9	0.88	65
64	Sample B/O	90/10	4.45	0.91	61
65	Sample A/O	70/30	4.8	1.9	92

*Not an example of the present invention when used alone.

We claim:

1. In a process for extrusion coating a substrate or for making a cast film with a thermoplastic composition, comprising the steps of:

(i) feeding a thermoplastic composition into at least one extruder,

(ii) melting and mixing the thermoplastic composition to form at least one uniform molten polymer stream, and

(iii) extruding the molten polymer stream through a die to form a primary web,

the improvement comprising:

(i) operating said extruder at line speeds greater than 152 meters/minute, and either

(a) drawing down said web onto said substrate to thereby coat said substrate with at least one layer of said thermoplastic composition, or

(b) cooling and drawing down said web onto a take-off device to make said film with at least one layer of said thermoplastic composition,

(ii) conveying or collecting said coated substrate or said film for subsequent use, and

(iii) using as said thermoplastic composition:

(I) from about 10 to 100 percent by weight of at least one substantially linear ethylene polymer characterized as having:

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

(b) a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leqq (I_{10}/I_2) - 4.63$,

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

(d) a single melting peak as determined using differential scanning calorimetry; and

(II) from 0 to about 90 percent by weight of at least one polymer selected from the group consisting of a heterogeneous linear ethylene polymer and high pressure ethylene polymer.

2. The process defined in claim 1 wherein (I) is an ethylene homopolymer.

3. The process defined in claim 1 wherein (I) is an interpolymer of ethylene and at least one C_3-C_{20} α-olefin.

4. The process defined in claim I wherein (I) is a copolymer of ethylene and one C_3-C_{20} α-olefin.

5. The process defined in claim 1 wherein (I) is a terpolymer of ethylene and two C_3-C_{20} α-olefins.

6. The process defined in claim I wherein the Dow Rheology Index (DRI) of (I) is at least 0.1.

7. The process defined in claim 1 wherein (I) has a melt index, I_2, from about 1 grams/10 minutes to about

10 grams/10 minutes, a density from about 0.9 grams/cm^3 to about 0.94 grams/cm^3, a molecular weight distribution, M_w/M_n, from about 1.5 to about 6.5, a melt flow ratio, I_{10}/I_2, of about 8 to about 12, a DRI of at least 0.1, and a draw ratio of at least about 18.

8. The process defined in claim **1** wherein (II) is an interpolymer of ethylene and at least one C_3-C_{20} α-olefin.

9. The process defined in claim **1** wherein (II) is a copolymer of ethylene and one C_3-C_{20} α-olefin.

10. The process defined in claim **1** wherein (II) is linear low density polyethylene.

11. The process defined in claim **1** wherein (II) is ultra low density polyethylene.

12. The process defined in claim **1** wherein (II) is low density polyethylene.

13. The process defined in claim **1** wherein (II) is an interpolymer of ethylene and at least one α,β-ethylenically unsaturated comonomer.

14. The process defined in claim **1** wherein (II) is a copolymer of ethylene and one α,β-ethylenically unsaturated comonomer.

15. The process defined in claim **1** wherein (II) is a copolymer of ethylene with acrylic acid.

16. The process defined in claim **1** wherein (II) is a copolymer ethylene with methyl acrylate.

17. The process defined in claim **1** wherein (II) is at least one high pressure ethylene polymer.

18. The process defined in claim **1** wherein (II) is at least one linear ethylene polymer.

19. The process defined in claim **1** wherein said composition is a ternary blend comprising at least one substantially linear ethylene polymer and at least one high pressure ethylene polymer and at least one linear ethylene polymer.

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