EXHIBIT 1

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United States Patent [19]

Chum et al.

[11] Patent Number: 5,847,053

[45] Date of Patent: Dec. 8, 1998

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

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

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

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

Related U.S. Application Data

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

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

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

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

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[57] **ABSTRACT**

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

16 Claims, 2 Drawing Sheets

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FIGURE 1

SLOPE OF STRAIN-HARDENING COEFFICIENT (S.H.C.) VS. DENSITY

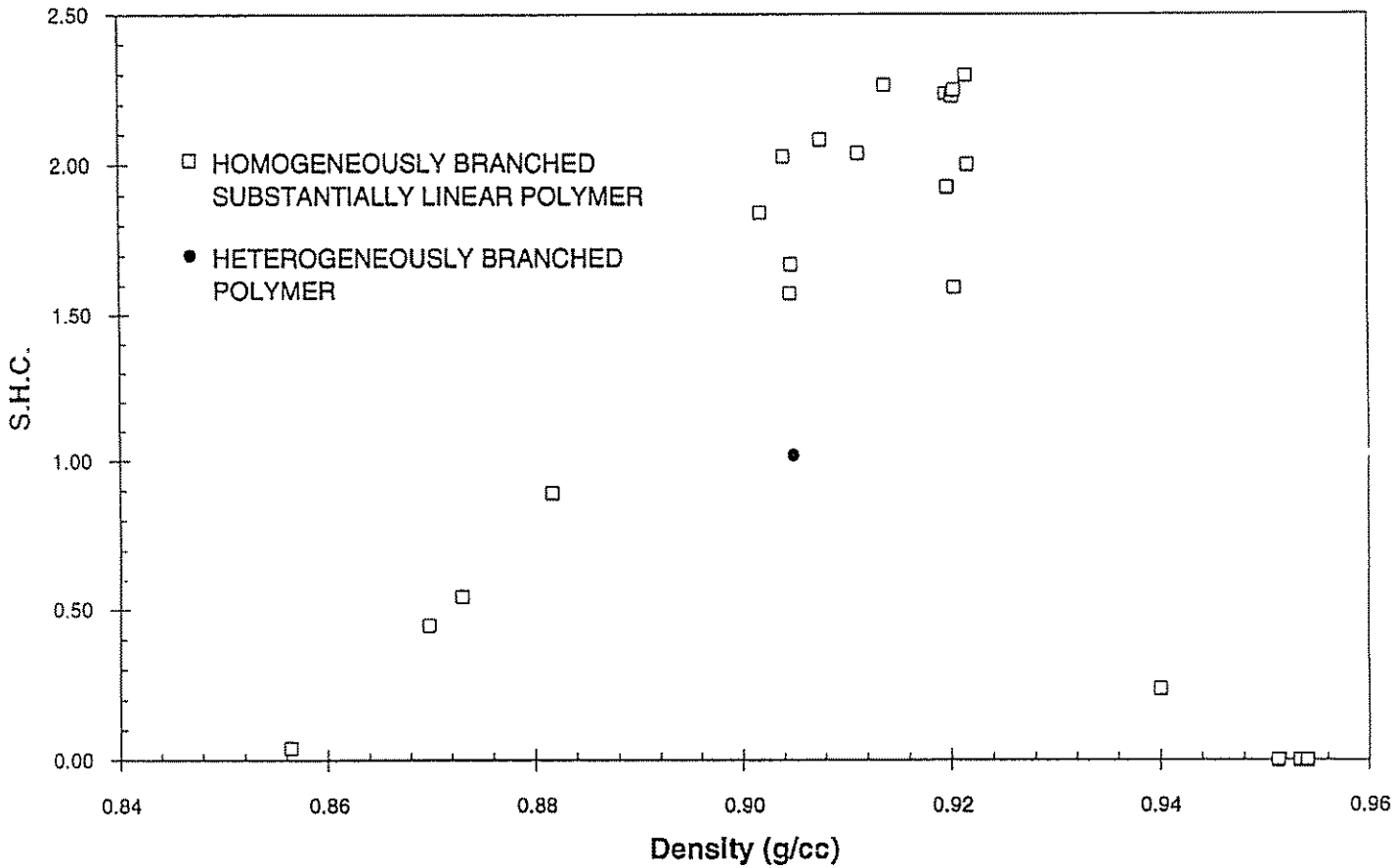
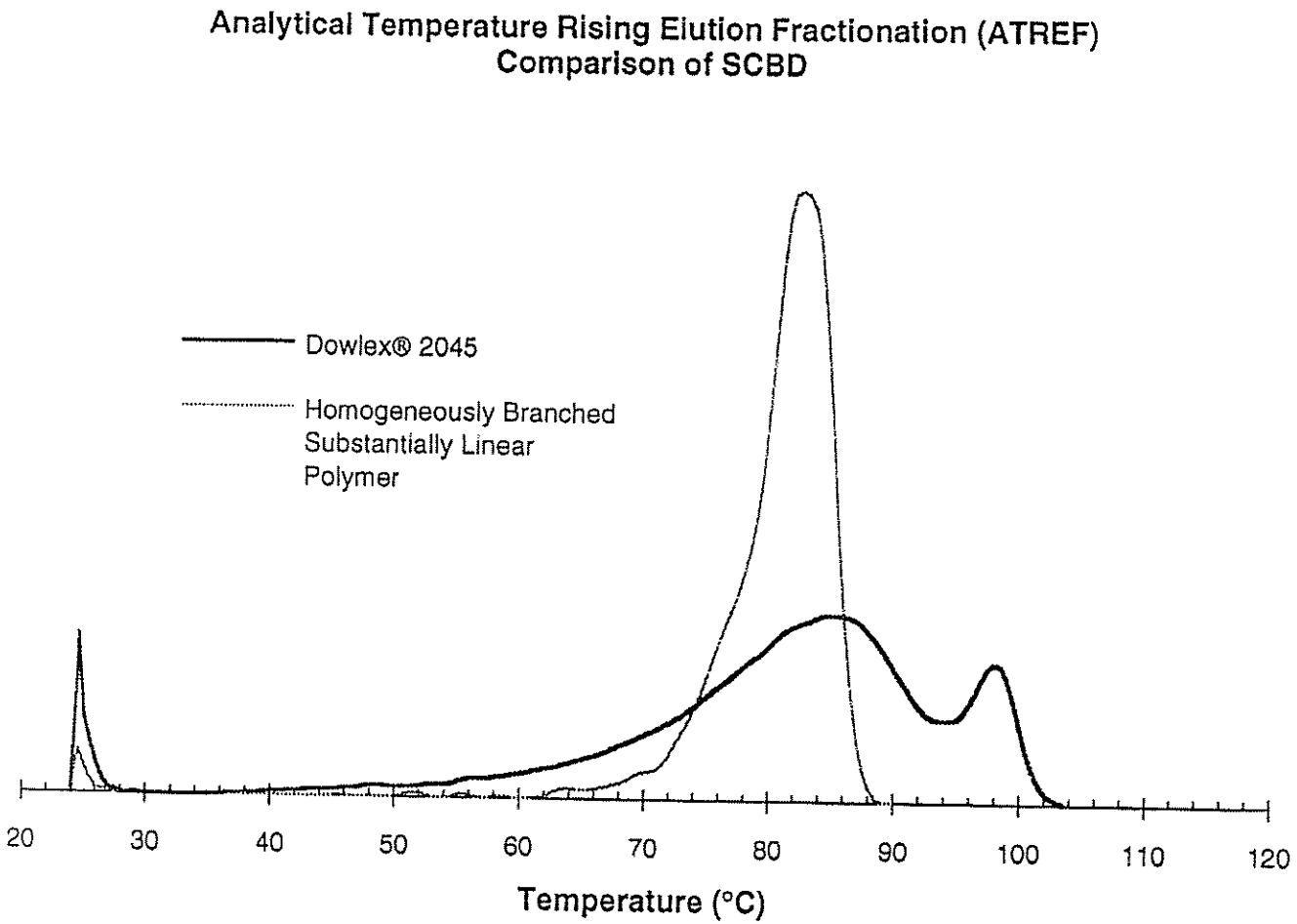


Figure 2


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

ETHYLENE POLYMER FILM MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

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

FIELD OF THE INVENTION

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

The polymer blends preferably comprise:

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

(B) a heterogeneously branched ethylene polymer.

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

BACKGROUND OF THE INVENTION

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

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

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

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

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

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

SUMMARY OF THE INVENTION

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

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

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

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

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

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

(iv) no linear polymer fraction, and

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

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

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

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

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

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

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

(iv) no linear polymer fraction, and

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

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

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

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

DETAILED DESCRIPTION OF THE INVENTION

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

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

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

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

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

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

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

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

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

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./2.16 kg (formerly known as

"Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The lower melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

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

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

Molecular Weight Distribution Determination

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

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

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

In this equation, a=0.4316 and b=1.0. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w=\Sigma w_i*M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the ith fraction eluting from the GPC column.

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

Determination of the Slope of Strain Hardening Coefficient

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

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

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

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

where I_2=melt index in grams/10 minutes.

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

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

TABLE 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0 8564	7 36	0 004
B	1 03	0 8698	7 46	0 45
C	0.57	0 873	7 22	0 54
D	1 01	0 8817	7 36	0 89
E	1 06	0 9018	7 61	1 84
F	2 61	0 9041	8 07	2 03
G	0.77	0 9047	9 01	1 57
H	9 82	0 9048	7 03	1 67
I	4 78	0 9077	7 18	2 08
J	3 13	0 9113	7 67	2 04
K	2 86	0 9139	7 87	2 27
L	1 08	0 9197	8 07	2 24
M	0 96	0 9198	9 61	1 93
N	0 99	0 9203	9 09	2 23
O	1 11	0 9204	10.15	1 59
P	1 06	0 9205	9 08	2 25
Q	1 12	0 9216	8.94	2 3
R	30 74	0 9217	6.27	2
S	31 58	0 94	6 02	0 24
T	0 97	0 9512	12 11	0
U	0 97	0 9533	10.5	0
V	0 92	0 954	7 39	0
W**	0 8	0 905	8.7	1 02

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

The Heterogeneously Branched Ethylene Polymer

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

Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene) The amount of each of these fractions varies depending upon the whole polymer properties desired For example, linear homopolymer polyethylene has neither branched nor highly branched fractions, but is linear A very low density heterogeneous polyethylene having a density from about 0 9 g/cm^3 to about 0 915 g/cm^3 (such as Attane® copolymers, sold by The Dow Chemical Company and Flexomer® sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer

Heterogeneously branched LLDPE (such as Dowlex® sold by The Dow Chemical Company) has a lower amount of the highly branched fraction, but has a greater amount of the medium branched fraction FIG 2 graphically depicts the relative amounts of these various fractions (as measured using temperature rising elution fractionation) for Dowlex® 2045 (a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0 92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7 93 and a molecular weight distribution (M_w/M_n) of about 3 34), as compared with a homogeneously branched substantially linear ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0 92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10 5 and a molecular weight distribution (M_w/M_n) of about 2 18 Note that the homogeneously branched polymer has a single relatively narrow peak at an elution temperature of about 85° C , while the Dowlex® 2045 polymer has a broad branching distribution, as represented by the breadth of elution temperatures over which the polymer fractions elute Dowlex® 2045 also has a distinct peak at an elution temperature of about 98° C , indicating the "linear" fraction of the whole polymer Increasing the fraction of the polymer which has the beneficial properties, without concomitantly increasing other fractions has not been demonstrated here-to-fore

Preferably, however, the heterogeneously branched ethylene polymer is a heterogeneously branched Ziegler polymerized ethylene/α-olefin interpolymer having no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1 3

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

(i) a density from about 0 93 g/cm^3 to about 0 965 g/cm^3,
(ii) a melt index (I_2) from about 0 1 g/10 min to about 500 g/10 min, and
(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1 3

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

The Formulated Compositions

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

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

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i e , branching) distribution, selecting the fraction having the specified properties (e g , SHC≧1 3), and blending the selected fraction in the appropriate amounts with another ethylene polymer This method is obviously not as economical as the in-situ interpolymerizations of U S Ser No 08/010,958, but can be used to obtain the compositions of the invention

Fabricated Articles Made from the Novel Compositions

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

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

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

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

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

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

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

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

EXAMPLE 1

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0 91 g/cm^3, I_{10}/I_2 of about 10, M_w/M_n of about 2, and SHC of about 1 81 is dry blended and then melt blended with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0 935 g/cm^3, I_{10}/I_2 of about 7 8, and M_w/M_n of about 3 4 The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1 3 The dry blend is tumble blended in a 50 gallon drum for about 1 hour

The melt blend is produced in a ZSK 30 twin screw extruder (30 mm screw diameter) and is then fabricated into film The final blended composition has a density of about 0 919 g/cm^3

The blended composition is then fabricated into blown film having a thickness of about 1 mil on an Egan Blown Film Line having a 2 inch diameter screw, a 3 inch die and at a 2.5 inch blow up ratio (BUR), as described in Table 2 For all film samples in Examples 1, 2, 4, and 6 and for comparative examples 3, 5, and 7, the targeted gauge is about 1 mil, using a blow-up ratio (BUR) of 2 5:1, a LLDPE screw design is used, a die gap of 70 mils is used, and a lay flat of about 11 875 inches is used

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

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

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

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

where

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

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

12=inches/foot

T=film thickness (inches), and

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

EXAMPLE 2

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

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

COMPARATIVE EXAMPLE 3

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

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

EXAMPLE 4

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

COMPARATIVE EXAMPLE 5

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

EXAMPLE 6

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

COMPARATIVE EXAMPLE 7

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

a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4 78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 8

Comparative example 8 is a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 minutes, a density of about 0 9249 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8 and a molecular weight distribution (M_w/M_n) of about 3 5.

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

TABLE 2

	Ex 1	Ex 2	Comp Ex 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp Ex. 8
Zone 1A (°F)	300	300	300	300	300	300	300	300
Zone 1B (°F)	450	451	475	474	475	475	475	474
Zone 1C (°F)	450	450	475	475	475	475	475	475
Zone 2A (°F)	450	450	475	474	475	475	475	475
Zone 2B (°F)	450	450	455	475	475	475	475	475
Zone 2C (°F)	450	450	475	475	475	475	475	475
Zone 3 (°F.)	451	452	474	477	477	476	476	474
Zone 4 (°F.)	450	450	473	475	475	475	475	475
Zone 5 (°F.)	450	450	475	475	475	475	475	475
Melt temp (°F)	475	477	515	501	502	499	499	497
Blower Air temp. (°F.)	47.3	45.7	57	44 4	86.5	47.6	NA	473
Chill Water temp. (°F.)	39	37.6	51 1	38 3	86.8	40	38 7	40 5
Extruder Die press. (psi)	2843	3427	1321	1874	1763	2883	2525	1952
Nozzle press (in)	3 2	4 5	4.38	4 4	4 9	4 6	4 6	4 3
Amps	27 3	33.1	37 7	39 9	40 2	50.1	42.6	38 6
Extruder speed (rpm)	27 6	28.8	21 5	23 1	21.1	21.5	22 1	21 7
Nip Roll speed (rpm)	33 1	36.9	39	39.8	36 2	37	36	37 8
Output (lbs/hr)	31	NR*	38 3	39	NR*	36	36	36
Frostline height (in.)	12 5	9	13	12	12	10 5	11	10 5

*NR = Not recorded

TABLE 3

	Ex 1	Ex 2	Comp Ex 3	Ex. 4	Comp. Ex 5	Ex. 6	Comp.. Ex. 7	Comp Ex 8
Yield (MD*) (psi)	1605	1595	1643	2040	2243	1973	1810	1782
Tensile (MD*) (psi)	8522	9525	7444	7794	7931	9325	8455	4928
Toughness (MD*) (ft-lbs/in^3)	1689	1773	1439	1671	1519	NR	NR	NR
Yield (CD**) (psi)	1530	1489	1706	2267	2407	1997	1809	1832
Tensile (CD**) (psi)	6252	7603	5807	7079	7458	7153	6326	4598
Toughness (CD**) (ft-lbs/in^3)	1282	1599	1358	1656	1495	NR	NR	NR
Elmendorf B (MD*) (grams)	288	216	334	317	194	320	398	297
Elmendorf B (CD**) (grams)	621	566	413	630	664	640	621	527
PPT Tear (MD*) (lbs)	6.79	6 18	5 99	6 2	6 5	6.2	6 2	5 3
PPT Tear (CD**) (lbs.)	7 44	7 42	6.46	6 8	8 1	7 0	7.5	6.1
Dart Impact A (grams)	708	610	354	410	186	412	186	164
Puncture (ft-lbs/in^3)	316	349	251	231	256	250	227	237
Film Block g.	75	33	87	32	17	11.8	17	22
Film Gradient Density (g/cm^3)	0 9145	0 9153	0.9155	0 9205	0 9218	0.9198	0 9201	0.9207
Film Gauge (low) (mils)	0 9	0 9	0.9	0 85	0 8	0.98	0.95	1 05
Film Gauge (high) (mils)	1 2	1.05	1 1	0 95	1	1 08	1 05	1 15

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

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

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

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

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

We claim:

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

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

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

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

(iv) no high density fraction,

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

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

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

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

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

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

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

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

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

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

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

(iv) no high density fraction,

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

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

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

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

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

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

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

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

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

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

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

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

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

* * * * *

EXHIBIT 2

US006111023A

United States Patent [19]

Chum et al.

[11] Patent Number: 6,111,023

[45] Date of Patent: *Aug. 29, 2000

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

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

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/927,393**

[22] Filed: **Aug. 27, 1997**

Related U.S. Application Data

[63] Continuation of application No. 08/544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of application No. 08/378,998, Jan. 27, 1995, abandoned, which is a continuation of application No. 08/054,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of application No. 07/776,130, Oct. 15, 1991, Pat. No. 5,272,236, which is a continuation-in-part of application No. 07/939,281, Sep. 2, 1992, Pat. No. 5,278,272.

[51] **Int. Cl.**[7] **C08L 23/06**

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

[58] **Field of Search** 525/240, 242, 525/320; 526/160, 161, 352

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[57] **ABSTRACT**

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

16 Claims, 2 Drawing Sheets

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FIG. 1

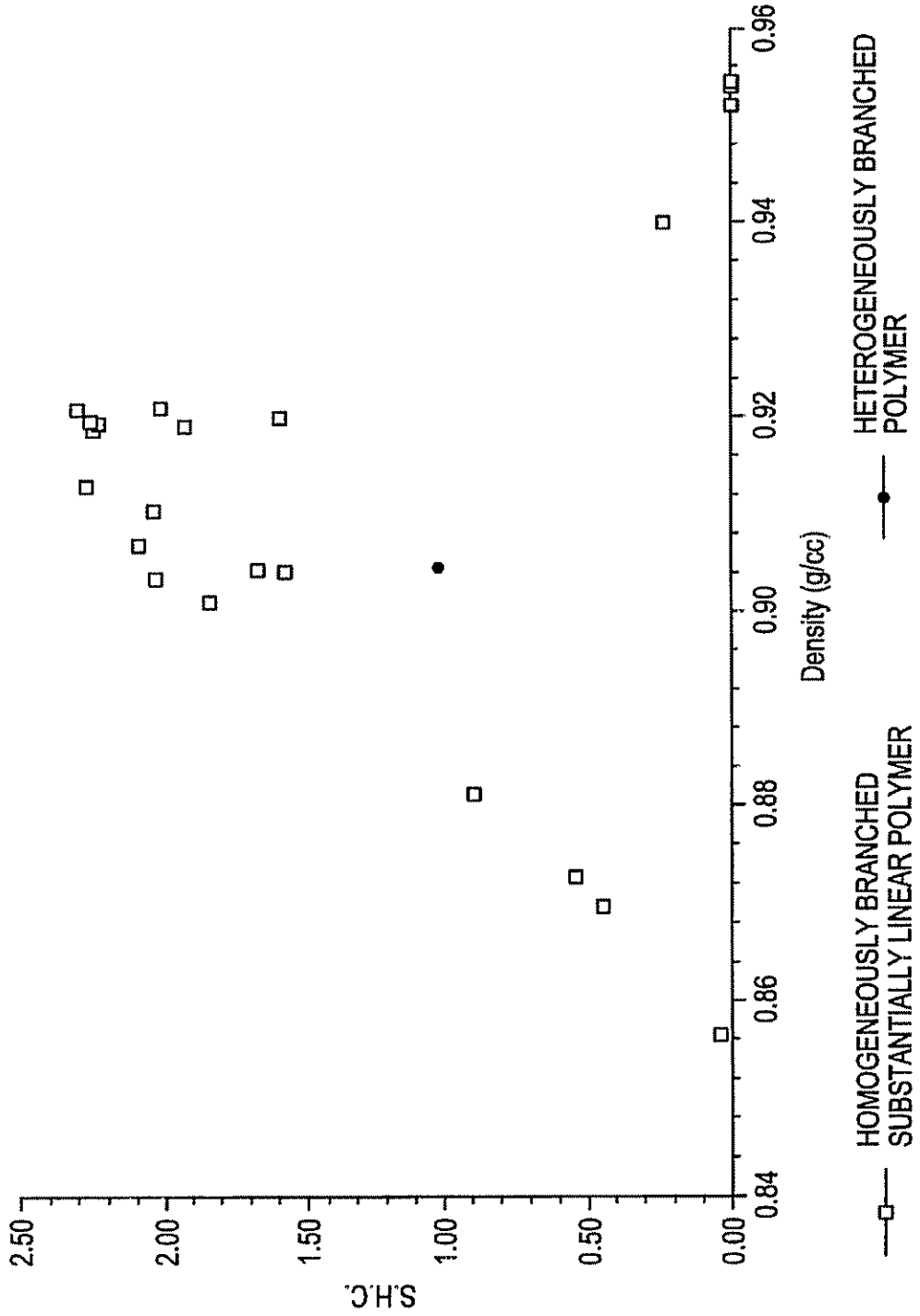
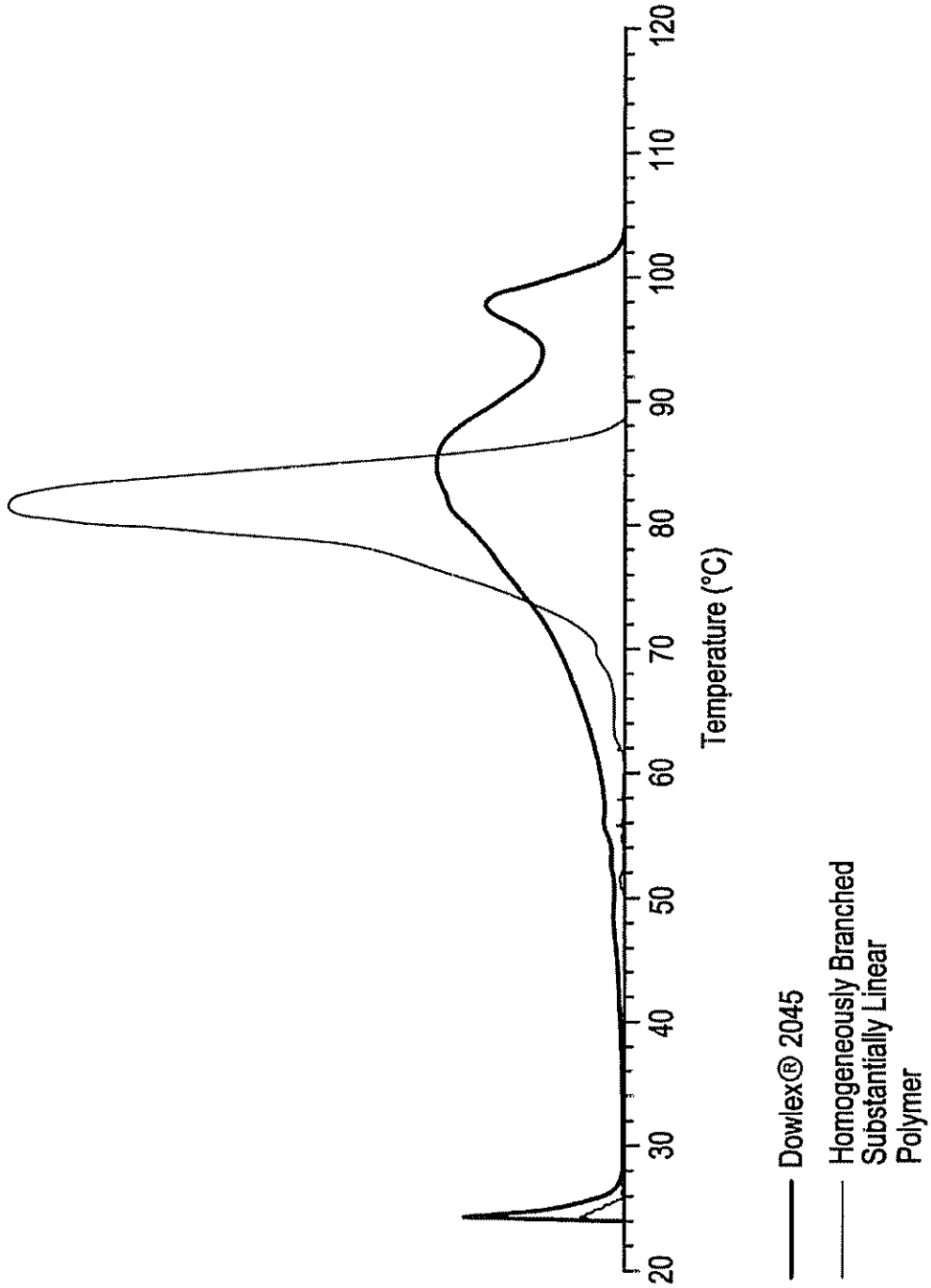

SCBDI
2.50
2.00
1.50
1.00
0.50
0.00
0.84
0.86
0.88
0.90
0.92
0.94
0.96
Density (g/cc)
HETEROGENEOUSLY BRANCHED POLYMER
HOMOGENEOUSLY BRANCHED SUBSTANTIALLY LINEAR POLYMER

FIG. 2


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

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Rule 1 60 continuation application of application Ser. No. 08/544,497, now U S. Pat. No. 5,677, 383, filed Oct. 18, 1995 as a Rule 1 60 continuation application of abandoned application Ser. No. 08/378,998, filed Jan. 27, 1995 as a Rule 1.62 continuation application of abandoned application Ser. No. 08/054,379, filed Apr. 28, 1993 as a continuation-in-part application of application Ser No. 07/776,130, filed Oct. 15, 1991, now U.S. Pat. No. 5,272,236 and as a continuation-in-part application of application Ser. No. 07/939,281, filed Sep. 2, 1992, now U S. Pat No. 5,278,272. This application is also related to application Ser. No. 08/834,050, filed Apr. 11, 1997, now issued U S Pat. No. 5,847,053. The disclosures of each of the above are incorporated herein, in their entireties, by reference. This application is also related to pending application Ser. No 08/010,958, filed Jan. 29, 1993 in the names of Brian W. S Kolthammer and Robert S. Cardwell and entitled Ethylene Interpolymerizations, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to compositions comprising specific ethylene/α-olefin polymer blends. The polymer blends preferably comprise,:

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

(B) a heterogeneously branched ethylene polymer.

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

BACKGROUND OF THE INVENTION

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

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

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

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

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

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

SUMMARY OF THE INVENTION

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

The compositions comprise (A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

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

(ii) a molecular weight distribution (M_w/M_n) from about 1 8 to about 2 8,

(iii) a melt index (I_2) from about 0 001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

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

(B) at least one heterogeneously branched ethylene polymer having a density from about 0 93 g/cm^3 to about 0.965 g/cm^3.

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

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

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

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2 8,

(iii) a melt index (I_2) from about 0 001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

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

(B) at least one heterogeneously branched ethylene polymer having a density from about 0 93 g/cm^3 to about 0 965 g/cm^3

Preferably, both the homogeneously branched substantially linear ethylene/α-olefin interpolymer and the homogeneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.3.

DETAILED DESCRIPTION OF THE INVENTION

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

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

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

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

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

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

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

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

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

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM

D-1238, Condition 190° C./2.16 kg (formerly known as "Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The lower melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

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

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

MOLECULAR WEIGHT DISTRIBUTION DETERMINATION

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

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

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

In this equation, a=0.4316 and b=1.0. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w = R\, w_i^* M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the ith fraction eluting from the GPC column.

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

DETERMINATION OF CRITICAL SHEAR STRESS AND CRITICAL SHEAR RATE

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

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

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

DETERMINATION OF THE SLOPE OF STRAIN HARDENING COEFFICIENT

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

such that the interior portion of the dogbone test piece has a width of 0.09 inches and a length of 0.197 inches.

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

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

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

where I_2=melt index in grams/10 minutes.

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

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

TABLE 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0.8564	7.36	0.004
B	1.03	0.8698	7.46	0.45
C	0.57	0.873	7.22	0.54
D	1.01	0.8817	7.36	0.89
E	1.06	0.9018	7.61	1.84
F	2.01	0.9041	8.07	2.03
G	0.77	0.9047	9.01	1.57
H	9.82	0.9048	7.03	1.67
I	4.78	0.9077	7.18	2.08
J	3.13	0.9113	7.67	2.04
K	2.86	0.9139	7.87	2.27
L	1.08	0.9197	8.07	2.24
M	0.96	0.9198	9.61	1.93
N	0.99	0.9203	9.09	2.23
O	1.11	0.9204	10.15	1.59
P	1.06	0.9205	9.08	2.25
Q	1.12	0.9216	8.94	2.3
R	30.74	0.9217	6.27	2
S	31.58	0.94	6.02	0.24
T	0.97	0.9512	12.11	0
U	0.97	0.9533	10.5	0
V	0.92	0.954	7.39	0
W**	0.8	0.905	8.7	1.02

*SHC = Slope of Strain Hardening Coefficient

**A comparative heterogeneously branched ethylene/1-octene copolymer

THE HETEROGENEOUSLY BRANCHED ETHYLENE POLYMER

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

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

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

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

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

(i) a density from about 0 93 g/cm^3 to about 0 965 g/cm^3,

(ii) a melt index (I_2) from about 0 1 g/10 min to about 500 g/10 min, and

(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1 3

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

THE FORMULATED COMPOSITIONS

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

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

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i e , branching) distribution, selecting the fraction having the specified properties (e g , SHC≧1 3), and blending the selected fraction in the appropriate amounts with another ethylene polymer This method is obviously not as economical as the in-situ interpolymerizations of U.S. Ser. No. 08/010,958, but can be used to obtain the compositions of the invention.

FABRICATED ARTICLES MADE FROM THE NOVEL COMPOSITIONS

Many useful fabricated articles benefit from the novel compositions disclosed herein. For example, molding operations can be used to form useful fabricated articles or parts from the compositions disclosed herein, including various injection molding processes (e g , that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264–268, "Introduction to Injection Molding" by H. Randall Parker and on pp. 270–271, "Injection Molding Thermoplastics" by Michael W. Green, the disclosures of which are incorporated herein by reference) and blow molding processes (e g , that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp 217–218, "Extrusion-Blow Molding" by Christopher Irwin, the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion (e g , pipes) and the like. Rotomolded articles can also benefit from the novel compositions described herein. Rotomolding techniques are well known to those skilled in the art and include, for example, those described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 296–301, "Rotational Molding" by R L. Fair, the disclosure of which is incorporated herein by reference).

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

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

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

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

films can also go through other post extrusion techniques, such as a biaxial orientation process

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

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

EXAMPLE 1

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

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

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

Film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples. Dart impact (type A) of the films is measured in accordance with ASTM D-1709-85; tensile strength, yield, toughness, and 2% secant modulus of the films is measured in accordance with ASTM D-882; Elmendorf tear (type B) is measured in accordance with ASTM D-1922; PPT tear is measured in accordance with ASTM D-2582; Block is measured in accordance with ASTM D-3354.

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

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

where

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

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

12=inches/foot

T=film thickness (inches), and

A=area of the film sample in the damp=12.56 in^2

EXAMPLE 2

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 0.5 g/10 min, density of about 0.915 g/cm^3, I_{10}/I_2 of about 11, M_w/M_n of about 2.4, and SHC of about 2.265 is dry blended and then melt blended (as described in Example 1) with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The final blended composition has a density of about 0.92 g/cm^3.

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

COMPARATIVE EXAMPLE 3

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

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

EXAMPLE 4

Example 4 is an in-situ blend made according to U.S. Ser. No. 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a melt index (I_2) of about 0.5 g/10 min., and a density of about 0.9054 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8.27 and a molecular weight distribution (M_w/M_n) of about 1.979 and comprises about

50% (by weight of the total composition). A heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 1.5 g/10 min, and a density of about 0.944 g/cm^3 and comprises the remaining 50% (by weight of the total composition). The total composition has a melt index (I_2) of about 1 g/10 min, a density of about 0.9248 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.22 and a molecular weight distribution (M_w/M_n) of about 2.641. This composition is made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 5

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

EXAMPLE 6

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

COMPARATIVE EXAMPLE 7

Comparative Example 7 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, the disclosure of which is incorporated herein by reference. About 25% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.49 g/10 min, a density of about 0.9244 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4.78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 8

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

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

TABLE 2

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

*NR = Not recorded

TABLE 3

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

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

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

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

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

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

We claim:

1. An ethylene polymer composition comprising

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one ethylene interpolymer having:

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

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

(iii) a slope of strain hardening coefficient greater than or equal to 1.3, and

(iv) a Composition Distribution Branch Index (CDBI) greater than 50 percent; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique.

2. The composition of claim 1 wherein the ethylene interpolymer (A) has a slope of strain hardening coefficient greater than or equal to 1.5.

3. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography.

4. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

5. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a single melting point, as determined using differential scanning calorimetry.

6. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

7. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and a single melting point as determined using differential scanning calorimetry

8. The composition of claim 1 or claim 3 wherein the ethylene interpolymer (A) is further characterized as having a no high density polymer fraction, as determined using a temperature rising elution fractionation technique, and a single melting point, as determined using differential scanning calorimetry.

9. A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one ethylene interpolymer having:

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

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

(iii) a slope of strain hardening coefficient greater than or equal to 1.3, and

(iv) a Composition Distribution Branch Index (CDBI) greater than 50 percent; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique.

10. The film of claim 9 wherein the ethylene interpolymer (A) has a slope of strain hardening coefficient greater than or equal to 1.5.

11. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography.

12. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

13. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a single melting point, as determined using differential scanning calorimetry.

14. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

15. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and a single melting point as determined using differential scanning calorimetry.

16. The film of claim 9 or claim 11 wherein the ethylene interpolymer (A) is further characterized as having a no high density polymer fraction, as determined using a temperature rising elution fractionation technique, and a single melting point, as determined using differential scanning calorimetry.

* * * * *

EXHIBIT 3

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

THE DOW CHEMICAL COMPANY, Plaintiff, v. NOVA CHEMICALS CORPORATION (CANADA) and NOVA CHEMICALS INC. (DELAWARE), Defendants.	)	C.A. No. 05-737 (JJF)

AMENDED REPLY TO COUNTERCLAIMS OF DEFENDANTS NOVA CHEMICALS CORPORATION AND NOVA CHEMICALS INC.

Plaintiff, The Dow Chemical Company ("Dow"), files this Reply in response to the Counterclaims dated August 10, 2006, filed by Defendants, NOVA Chemicals Corporation and NOVA Chemicals Inc. (collectively "NOVA").

REPLY

COUNTERCLAIMS

PARTIES AND JURISDICTION

1. NOVA Chemicals Corporation is a corporation organized under the laws of Canada with a principal place of business at 1000 Seventh Avenue S.W., Calgary, Alberta T2P SC6, Canada.

Answer:

Upon information and belief, Plaintiff admits the allegation.

2. NOVA Chemicals Inc. is a corporation organized under the laws of Delaware with a principal place of business at Westpointe Center, 1550 Caraopolis Heights Road, Moon Township, Pennsylvania 15108.

Answer:

Upon information and belief, Plaintiff admits the allegation.

3. On information and belief, Dow is a corporation organized under the laws of Delaware with a principal place of business at 2030 Dow Center, Midland, Michigan 48674.

Answer:

Admitted.

4. This Court has jurisdiction over these Counterclaims pursuant to at least 28 U.S.C. §§ 1331, 1338, 1367, and 2201.

Answer:

Admitted.

5. Dow is subject to personal jurisdiction in this judicial district for the present Counterclaims, at least because it commenced the present action and because, upon information and belief, it is a Delaware corporation.

Answer:

Admitted.

6. These Counterclaims are for declaratory judgment relief arising under 28 U.S.C. §§ 2201 and 2202, and the patent law of the United States, 35 U.S.C. § 101 *et seq.*

Answer:

Admitted.

COUNTERCLAIM I: DECLARATORY JUDGMENT OF NO INFRINGEMENT OF THE '053 PATENT

7. NOVA adopts and incorporates in this Counterclaim paragraphs 1-6 above, as if set forth herein.

Answer:

Plaintiff's answers for paragraphs 1-6 are incorporated, as if set forth herein.

8. Claim 1 of the '053 patent is addressed to a "film made from an ethylene polymer composition," the composition comprising, *inter alia*, "at least one heterogeneously branched linear ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965g/cm^3."

Answer:

Admitted that the quoted language appears in U.S. Patent No. 5,847,053, issued on December 8, 1998 ("the '053 patent"). The term "addressed" is vague and ambiguous in its usage in this paragraph. To the extent "addressed" means that claim 1 in its preamble refers to such a film, admitted.

9. Claim 6 of the '053 patent is addressed to "An ethylene polymer composition comprising," *inter alia*, "at least one heterogeneously branched linear ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965g/cm^3."

Answer:

Admitted that the quoted language appears in the '053 patent. The term "addressed" is vague and ambiguous in its usage in this paragraph. To the extent "addressed" means that the preamble of Claim 6 refers to such an ethylene polymer composition, admitted.

10. Claims 1 and 6 of the '053 patent are the only independent claims of the '053 patent.

Answer:

Admitted.

11. The '053 patent states, *inter alia,* at column 7, lines 28-30 that "The ethylene polymer to be combined with the homogenous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer...."

Answer:

Admitted.

12. On information and belief, prior to filing its Complaint in the present action, Dow did not have information showing that any accused NOVA SURPASS® product contains a heterogeneously branched polymer, as that term is used in the '053 patent.

Answer:

Denied.

13. On information and belief, prior to serving its Complaint in the present action, Dow had information that NOVA SURPASS® products do not contain a heterogeneously branched polymer, as that term is used in the '053 patent.

Answer:

Denied.

14. The '053 patent states, *inter alia,* in column 7, lines 33-36 that "Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution."

Answer:

Admitted.

15. The '053 patent states, *inter alia,* in column 7, lines 36-41 that "heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)."

Answer:

Admitted.

16. On information and belief, prior to filing its Complaint in the present action, Dow did not identify a polymer component in any accused NOVA SURPASS® product as having "a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)," as those terms are used in the '053 patent.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '053 patent." The claims of the patent do not require there be a polymer component in any accused NOVA SURPASS® product as having "a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '053 patent in any NOVA SURPASS® polymer, denied.

17. The '053 patent states, *inter alia,* at column 7, lines 57 - 66 that Dowlex® 2045 is "a heterogeneously branched ethylene/1-octene copolymer...."

Answer:

Admitted.

18. The '053 patent states, *inter alia,* at column 8, lines 4-7 that "Dowlex® 2045 also has a distinct peak at an elution temperature of about 98°C., indicating the 'linear' fraction of the whole polymer."

Answer:

Admitted.

19. On information and belief, prior to filing its Complaint in the present action, Dow did not measure "a distinct peak at an elution temperature of about 98°C," as those terms are used in the '053 patent, for any accused NOVA SURPASS® product.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '053 patent." The claims of the patent do not require the measurement of "a distinct peak at an elution temperature of about 98°C." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '053 patent in any NOVA SURPASS® polymer, denied.

20. The '053 patent states, *inter alia,* at column 8, lines 23-26 that "The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)."

Answer:

Admitted.

21. On information and belief, prior to filing its Complaint in the present action, Dow did not identify in any accused NOVA SURPASS® product any interpolymers and/or copolymers that "have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)," as those terms are used in the '053 patent.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '053 patent." The claims of the patent do not require that there be in any accused product any interpolymers and/or copolymers that "have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '053 patent in any NOVA SURPASS® polymer, denied.

22. During the prosecution leading to the '053 patent, Dow distinguished its claimed products from blends of multiple homogeneous polymers.

Answer:

Denied.

23. On information and belief, prior to serving its Complaint in the present action, Dow had information that SURPASS® products contain only "homogenously branched" copolymers, as those terms are used in the '053 patent.

Answer:

Denied.

24. On information and belief, Dow served its complaint in this action knowing that NOVA did not infringe the '053 patent.

Answer:

Denied.

25. NOVA has not infringed and is not infringing the '053 patent with its SURPASS® polyethylene products, either directly, contributorily, and/or by inducement.

Answer:

Denied.

26. NOVA is entitled to a declaratory judgment that it has not infringed and is not infringing the '053 patent with its SURPASS® polyethylene products, either directly, contributorily, and/or by inducement.

Answer:

Denied.

COUNTERCLAIM II: DECLARATORY JUDGMENT OF INVALIDITY OF THE '053 PATENT

27. NOVA adopts and incorporates in this Counterclaim paragraphs 1-6 above, as if set forth herein.

Answer:

Plaintiff's answers for paragraphs 1-6 are incorporated, as if set forth herein.

28. "Example 4" of the '053 patent is directed, *inter alia*, to an "in-situ blend... wherein the homogenously branched substantially linear polymer is made in a first reactor... [And a] heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor...."

Answer:

Admitted that the quoted language appears in the '053 patent. The phrase "directed, *inter alia*, to" is vague and ambiguous in its usage in this paragraph. To the extent "directed, *inter alia*, to" is intended to mean that "Example 4" discloses an in-situ blend, admitted.

29. The '053 patent does not report a slope of strain hardening coefficient (SHC) value for the blend of "Example 4."

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses a slope of strain hardening coefficient (SHC) value for the blend of "Example 4."

30. The '053 patent does not report an SHC value for any component identified as a component of the blend of "Example 4."

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '053 patent combined with the presumed knowledge of a person

skilled in the art at the time of the effective filing date of the '053 patent discloses a slope of strain hardening coefficient (SHC) value for at least a component identified as a component of the blend of "Example 4."

31. The '053 patent does not report an SHC value for any component identified as a component of an in-situ blend.

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses a slope of strain hardening coefficient (SHC) value for at least a component of an in-situ blend.

32. The '053 patent does not provide conditions to separate an in-situ blend of polymers into components.

Answer:

The phrase "provide conditions" is vague and ambiguous as used in this paragraph. To the extent "provide conditions" means disclose how to identify the components of an in-situ blend of polymers, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses how to identify the components of an in-situ blend of polymers.

33. The '053 patent does not provide conditions to separate an in-situ blend of polymers into separate components where the polymer components have overlapping temperature rising elution fractionation (TREF) elution temperatures.

Answer:

The phrase "provide conditions" is vague and ambiguous as used in this paragraph. To the extent "provide conditions" means disclose how to identify the components of an in-situ blend of

polymers, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses how to identify the components of an in-situ blend of polymers where the polymer components have overlapping temperature rising elution fractionation (TREF) elution temperatures.

34. The '053 patent states, *inter alia*, at column 6, lines 40-42 that "FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening."

Answer:

Admitted.

35. The '053 patent states, *inter alia,* at column 6, lines 61-62 that "FIG. 1 graphically depicts the relationship between the density of the homogeneously branched substantially linear ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient."

Answer:

Admitted.

36. The '053 patent describes "FIG. 1" differently at column 6, lines 40-42 than at column 6, lines 61-62.

Answer:

The term "differently" is vague and ambiguous in its usage in this paragraph. Admitted that the text in the '053 patent at column 6, lines 40-42 is not identical to the text at column 6, lines 61-62.

37. The "FIG. 1" described in the '053 patent at column 6, lines 40-42 is not contained in the '053 patent.

Answer:

Admitted.

38. On information and belief, prior to April 28, 1993, at least one of the named inventors of the '053 patent was aware of a figure as described at column 6, lines 40-42 of the '053 patent.

Answer:

Upon information and belief, denied.

39. On information and belief, prior to April 28, 1993, at least one member of Dow's Patent Department who participated in the prosecution leading to the '053 patent was aware of a figure as described at Column 6, lines 40-42 of the '053 patent.

Answer:

Upon information and belief, denied.

40. The figure labeled "Figure 1" appearing on the fourth page of the issued '053 patent does not depict "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42.

Answer:

The term "depict" is vague and ambiguous in its usage in this paragraph. Admitted that Figure 1 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '053 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

41. The figure labeled "Figure 2" appearing on the fifth page of the issued '053 patent does not depict "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42.

Answer:

The term "depict" is vague and ambiguous in its usage in this paragraph. Admitted that Figure 2 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '053 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

42. The '053 patent does not contain a figure showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42.

Answer:

Admitted that no figure in the '053 patent expressly illustrates "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '053 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

43. A figure showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42, is necessary for the understanding of the subject matter claimed in the '053 patent.

Answer:

Denied.

44. The '053 patent states, *inter alia,* at column 6, line 67 that "Table 1 displays the data of FIG. 1 in tabular form:"

Answer:

Admitted.

45. The data contained in Table 1 of the '053 patent corresponds to the data of the "FIG. 1" described in the '053 patent at column 6, lines 61-67 and depicted on the fourth page of the '053 patent.

Answer:

Admitted.

46. The data contained in Table 1 of the '053 patent is not data showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42.

Answer:

The term "showing" is vague and ambiguous as used in this paragraph. Admitted that Table 1 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '053 patent at column 6, lines 40-42. Denied that the '053 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

47. Independent Claims 1 and 6 of the '053 patent contain a limitation requiring that component "A" have "a slope of strain hardening coefficient greater than or equal to 1.3."

Answer:

Denied. Under the doctrine of equivalents, claim limitations cover their literal scope and equivalent subject matter.

48. All claims of the '053 patent contain a limitation that component "A" have a "slope of strain hardening coefficient" at least greater than or equal to 1.3.

Answer:

Denied. Under the doctrine of equivalents, claim limitations cover their literal scope and equivalent subject matter.

49. The '053 patent states, inter alia, at column 6, lines 45-50 that:
The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

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

where I_2 =melt index in grams/10 minutes.

Answer:

Admitted.

50. The "slope of strain hardening" parameter appearing in the SHC equation defined in the '053 patent at column 6, lines 45-50 is disclosed to be determined using "FIG. 1," wherein "FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined."

Answer:

Denied.

51. A figure showing a "strain hardening region" is not present in the '053 patent.

Answer:

This paragraph is vague in that the phrase "strain hardening region" has no context. To the extent this paragraph seeks an admission that in none of the figures of the '053 patent is there a representation of a polymer with a strain hardening region, denied.

52. The determination of a "parallel line in the strain hardening region" is not disclosed in the '053 patent.

Answer:

Denied.

53. In the prosecution leading to the '053 patent, Dow did not cite any printed publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993 that contains the SHC definition at column 6, lines 45-50 of the '053 patent.

Answer:

Admitted that, upon information and belief, Plaintiff did not cite a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: $(slope\ of\ strain\ hardening)*(I_2)^{0.25}$ where I_2 =melt index in grams/10 minutes." In all other respects, denied. One or more printed publications cited by Plaintiff and/or the Examiner disclose information defining all parts of the equation as described at column 6, lines 45-50 of the '053 patent.

54. In the prosecution leading to the '053 patent, the Examiner did not cite any printed publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993 that contains the SHC definition at column 6, lines 45-50 of the '053 patent.

Answer:

Admitted that, upon information and belief, the Examiner did not cite a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: $(slope\ of\ strain\ hardening)*(I_2)^{0.25}$ where I_2 =melt index in grams/10 minutes." In all other respects, denied. One or more printed publications cited by Plaintiff and/or the Examiner disclose information defining all parts of the equation as described at column 6, lines 45-50 of the '053 patent.

55. On information and belief, Dow is not aware of any publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993, that contains the SHC definition at column 6, lines 45-50 of the '053 patent.

Answer:

Admitted that, upon information and belief, Plaintiff is not aware of a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: *(slope of strain hardening)*$(I_2)^{0.25}$* where I_2 =melt index in grams/10 minutes." In all other respects, denied. Plaintiff is aware of one or more printed publications from prior to April 28, 1993 that, singularly or combined, disclose information defining all parts of the equation as described at column 6, lines 45-50 of the '053 patent.

56. The '053 patent indicates that the I_2 parameter in the equation at column 6, lines 45-50 has the units of "grams/10 minutes."

Answer:

Admitted.

57. The '053 patent does not provide any units for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

Answer:

Admitted that '053 patent does not expressly state specific units to be used for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50. In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses units to be used for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

58. On information and belief, prior to April 28, 1993, at least one of the named inventors of the '053 patent was aware of units for the "slope of strain hardening" parameter, as that parameter is used in the '053 patent at column 6, lines 45-50.

Answer:

Admitted.

59. The '053 patent does not provide any units for the "SHC" parameter in the equation at column 6, lines 45-50.

Answer:

Admitted that '053 patent does not expressly state specific units to be used for the "SHC" parameter in the equation at column 6, lines 45-50. In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses units to be used for the "SHC" parameter in the equation at column 6, lines 45-50.

60. In the section of the '053 patent entitled "Determination of the Slope of Strain Hardening Coefficient" beginning at column 6, line 6, the '053 patent refers to both English units (*e.g.*, psi at column 6, line 12) and metric units (*e.g.*, grams/cm^3 at column 6, lines 57-58).

Answer:

Admitted.

61. The '053 patent does not state whether English or metric units should be used for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

Answer:

Admitted that there is no express statement stating whether English or metric units should be used at column 6, lines 45-50. In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the

'053 patent discloses whether English or metric units are appropriate for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

62. The '053 patent does not state what units should be used for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

Answer:

Admitted that there is no express statement stating whether specific units for the "slope of strain hardening" parameter should be used in the equation at column 6, lines 45-50. In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses what units should be used for the "slope of strain hardening" parameter in the equation at column 6, lines 45-50.

63. The '053 patent incorporates by reference patents that collectively use multiple different units for the slope of a stress/strain curve, including "lbs./in/ /oz./yd.^{2}" in United States Patent No. 3,458,706, "MPa" in United States Patent No. 4,597,920, "KPa" in United States Patent No. 5,059,481, "GPa" and "gm/denier" in United States Patent No. 4,413,110, "psi" in United States Patent No. 4,663,220, and "Kpsi" in United States Patent No. 4,865,902,

Answer:

Denied.

64. At column 27, lines 26-29 of U.S. Patent No. 4,413,110, the numerical value reported in units of "GPa" is different from the numerical value reported in "g/d."

Answer:

Admitted that at column 27, lines 26-29 of U.S. Patent No. 4,413,110, that patent states, "[t]he measurement 140 GPa (1587 g/d) . . ." and that the two numerical values "140" and "1587" are different.

65. The numerical value for the SHC parameter in the equation at column 6, lines 45-50 of the '053 patent depends on, *inter alia*, the units used for the "slope of strain hardening" parameter.

Answer:

The paragraph is vague and ambiguous in that no polymer is identified. Plaintiff interprets this paragraph to mean that the value for the SHC parameter for all polymers in all situations in the equation at column 6, lines 45-50 of the '053 patent depends on, *inter alia*, the units used for the "slope of strain hardening" parameter. Under this interpretation, denied.

66. The '053 patent does not specify units for the "slope of strain hardening" parameter.

Answer:

Denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses appropriate units for the "slope of strain hardening" parameter.

67. On November 1, 1999, the patent application leading to Dow's United States Patent No. 6,723,398 B1 ("the '398 patent") was filed in the United States Patent Office.

Answer:

Upon information and belief, admitted.

68. A true and correct copy of the '398 patent is attached hereto as Exhibit i.

Answer:

Upon information and belief, admitted.

69. The '398 patent states, *inter alia*, at column 2, lines 45-49 that "FIG. 2 shows the various regions of a typical tensile curve (as load in pounds versus extension in inches) and the particular region used to determine the slope of strain hardening."

Answer:

Admitted.

70. The '398 patent includes on page 4 "FIG. 2," which corresponds to the description in the '398 patent at column 2, lines 45-49.

Answer:

Admitted.

71. "FIG. 2" of the '398 patent shows "various stages of the stress/strain curve used to calculate the slope of strain hardening."

Answer:

This paragraph is vague and ambiguous in that no polymer is specified. Admitted that "FIG. 2" of the '398 patent illustrates "various stages of the stress/strain curve used to calculate the slope of strain hardening" for the polymers that are the subject of Figure 2 of the '398 patent. Denied that "FIG. 2" of the '398 patent shows "various stages of the stress/strain curve used to calculate the slope of strain hardening" for all polymers in all situations.

72. As depicted in "FIG. 2" of the '398 patent, the "Strain Hardening Region" begins before the "point of 10% extension before failure."

Answer:

Admitted that for the polymers that are the subject of "FIG. 2" of the '398 patent, the "Strain Hardening Region" may begin before the "point of 10% extension before failure." Denied, however, that all polymers would behave exactly as illustrated in "FIG. 2" of the '398 patent, or that the "Strain Hardening Region" begins before the "point of 10% extension before failure" for all polymers in all situations.

73. The '398 patent discloses that a subsection of the "strain hardening region" is used to determine the "slope of strain hardening."

Answer:

Admitted that for the polymers that are the subject of "FIG. 2" of the '398 patent, the '398 patent discloses that a subsection of the "strain hardening region" can be used to determine the "slope of strain hardening." Otherwise denied that the '398 patent discloses that a subsection of the "strain hardening region" is used to determine the "slope of strain hardening" for all polymers in all situations.

74. The '398 patent states, *inter alia*, at column 11, lines 6-11 that:

> The slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain).

Answer:

Denied.

75. The '053 patent does not disclose that the slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain).

Answer:

Admitted that the '053 patent does not expressly state that "the slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain)." In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at

the time of the effective filing date of the '053 patent discloses how to determine the slope of strain hardening.

76. The '398 patent states, *inter alia*, at column 11, lines 12-15 that:

> A more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point.

Answer:

Admitted.

77. The '053 patent does not disclose that a more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point.

Answer:

The '053 patent does not expressly state that "a more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point." In all other respects, denied. The '053 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '053 patent discloses how to determine the slope of strain hardening.

78. The '398 patent, at column 10, lines 61-64, identifies the "line parallel to the strain hardening region" as a "10 percent secant line."

Answer:

Denied.

79. The '053 patent does not identify the "line parallel to the strain hardening region" as a "10 percent secant line."

Answer:

Admitted.

80. The '053 patent does not identify any subsection of the "strain hardening region" from which the "slope of strain hardening," as those terms are used in the '053 patent, is or should be determined.

Answer:

Denied.

81. No drawing containing the information in "FIG. 2" of the '398 patent related to the region used to determine the "slope of strain hardening" or the units for "slope of strain hardening" is contained in the '053 patent.

Answer:

Admitted that there are no drawings in the '053 patent; there are only computer-generated figures.

82. ASTM dimensions for stress/strain curves in accordance with ASTM D-882 are pressure vs. % extension.

Answer:

This paragraph is vague and ambiguous. Pressure vs. % extension is not an expression of "dimensions." The term "ASTM dimensions" is vague and ambiguous as used in this paragraph. Plaintiff consequently lacks information, knowledge, and belief to either admit or deny this averment.

83. The slope of the strain hardening, as depicted in "FIG. 2" in the '398 patent, has units of "pounds/inch."

Answer:

Admitted.

84. The '053 patent does not disclose that "slope of strain hardening" should be in units of "pounds/inch."

Answer:

Denied.

85. The units "pounds/inch" do not correspond to the dimensions of pressure vs. % extension.

Answer:

The term "correspond" is vague and ambiguous as used in this paragraph. "Pressure vs. % extension" is not an expression of "dimensions." Denied that "pounds/inch" can never relate to "pressure vs. % extension."

86. On information and belief, one or more of the named inventors of the '053 patent was aware of the preferred subsection of the "strain hardening region" used to determine the "slope of strain hardening" and/or the units to be used in determining that parameter prior to April 28, 1993.

Answer:

This paragraph assumes a fact that Plaintiff denies, namely that there was a preferred subsection as of April 28, 1993, of the "strain hardening region" for all polymers in all circumstances or situations for use in determining the "slope of strain hardening." Denied.

87. On information and belief, one or more attorneys in Dow's Patent Department who participated in the prosecution leading to the '053 patent was aware of the preferred subsection of the "strain hardening region" used to determine the "slope of strain hardening" and/or units to be used in determining that parameter prior to April 28, 1993.

Answer:

This paragraph assumes a fact that Plaintiff denies, namely that there was a preferred subsection as of April 28, 1993, of the "strain hardening region" for all polymers in all circumstances or situations for use in determining the "slope of strain hardening." Denied.

88. On information and belief, at the time Dow served its complaint in this action, Dow knew that "FIG. 1" referred to at Column 6, lines 40-42 was not present in the '053 patent.

Answer:

This paragraph is vague and ambiguous in referring to whether "FIG. 1" "was present" in the '053 patent. To the extent this paragraph seeks an admission that a figure described at column 6, lines 40-42 could not be constructed by a person of ordinary skill in the art based on the disclosure of the '053 patent, denied.

89. On information and belief, at the time Dow served its complaint in this action, Dow knew that the '053 patent failed to disclose units for the "slope of strain hardening" parameter that appears in the SHC equation described at Column 6, lines 45-50.

Answer:

Assumes facts that Plaintiff denies: that the '053 patent failed to disclose units for the "slope of strain hardening" parameter that appears in the SHC equation described at Column 6, lines 45-50. Denied.

90. On information and belief, at the time Dow served its Complaint in this action, Dow knew that the use of different units for the "slope of strain hardening" parameter in the equation

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

would result in different SHC values when calculated using this equation.

Answer:

Assumes facts that Plaintiff denies: that different values for SHC would result for all polymers in all circumstances from the use of different units for the "slope of strain hardening" parameter. Denied.

91. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '053 patent failed to adequately disclose the SHC parameter recited in each claim of the '053 patent and/or failed to disclose the best mode for determining SHC because of the omission from the '053 patent specification of the "FIG. 1" referred to at column 6, lines 40-42.

Answer:

Assumes facts that Plaintiff denies: that Plaintiff's '053 patent failed to adequately disclose the SHC parameter recited in each claim of the '053 patent and/or failed to disclose the best mode for determining SHC because of the omission from the '053 patent specification of the "FIG. 1" referred to at column 6, lines 40-42. Denied.

92. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '053 patent failed to furnish a drawing necessary for the understanding of the subject matter sought to be patented.

Answer:

Assumes facts that Plaintiff denies: that Plaintiff's '053 patent failed to furnish a drawing necessary for the understanding of the subject matter sought to be patented. Denied.

93. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '053 patent failed to furnish any units for the "slope of strain hardening" parameter that appears in the SHC equation described at Column 6, lines 45-50, which units are necessary for calculation of SHC.

Answer:

The use of the term "furnish" in this paragraph is vague and ambiguous. To the extent this paragraph seeks an admission that Plaintiff knew that the units for the slope of strain hardening parameter are not disclosed in the '053 patent, then this paragraph assumes a fact that Plaintiff denies. Denied.

94. The claims of the '053 patent are invalid for failure to comply with the conditions for patentability specified by 35 U.S.C. § 101, *et seq.*, including sections 102, 103, 112, and/or 113.

Answer:

Denied.

COUNTERCLAIM III: DECLARATORY JUDGMENT OF NO INFRINGEMENT OF THE '023 PATENT

95. NOVA adopts and incorporates in this Counterclaim paragraphs 1-6 above, as if set forth herein.

Answer:

Plaintiff's answers for paragraphs 1-6 are incorporated, as if set forth herein.

96. Claim 1 of the '023 patent is addressed to "An ethylene polymer composition comprising," *inter alia*, "at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique."

Answer:

Admitted that the quoted language appears in U.S. Patent No. 6,111,023, issued on August 29, 2000 ("the '023 patent"). The term "addressed" is vague and ambiguous in its usage in this paragraph. To the extent "addressed" means that claim 1 in its preamble refers to such a polymer composition, admitted.

97. Claim 9 of the '023 patent is addressed to "A film made from an ethylene polymer composition, wherein the composition comprises," *inter alia*, "at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique."

Answer:

Admitted that the quoted language appears in the '023 patent. The term "addressed" is vague and ambiguous in its usage in this paragraph. To the extent "addressed" means that the preamble of Claim 9 refers to such a film, admitted.

98. Claims 1 and 9 of the '023 patent are the only independent claims of the '023 patent.

Answer:

Admitted.

99. During the prosecution leading to the '023 patent, Dow stated, *inter alia,* that "the term 'linear fraction' or 'linear polymer fraction' (at least as used in the present application) refers to heterogeneously branched ethylene polymers."

Answer:

Admitted that the quoted language appears as part of a broader statement made during prosecution. Denied that this incomplete quotation is the definition of the phrase "linear fraction" or "linear polymer fraction."

100. The '023 patent states, *inter alia,* at column 8, lines 13-16 that "The ethylene polymer to be combined with the homogenous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer...."

Answer:

Admitted.

101. On information and belief, prior to filing its Complaint in the present action, Dow did not have information showing that any accused NOVA SURPASS® product contains a heterogeneously branched polymer, as that term is used in the '023 patent.

Answer:

Denied.

102. On information and belief, prior to serving its Complaint in the present action, Dow had information that NOVA SURPASS® products do not contain a heterogeneously branched polymer, as that term is used in the '023 patent.

Answer:

Denied.

103. The '023 patent states, *inter alia,* in column 8, lines 19-22 that "Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution."

Answer:

Admitted.

104. The '023 patent states, *inter alia,* in column 8, lines 22 - 27 that "heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)."

Answer:

Admitted.

105. On information and belief, prior to filing its Complaint in the present action, Dow did not identify a polymer component in any accused NOVA SURPASS® product as having "a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)," as those terms are used in the '023 patent.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '023 patent." The claims of the patent do not require there be a polymer component in any accused NOVA SURPASS® product as having "a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene)." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '023 patent in any NOVA SURPASS® polymer, denied.

106. The '023 patent states, *inter alia,* at column 8, lines 43-45 that Dowlex® 2045 is "a heterogeneously branched ethylene/1-octene copolymer . . . ."

Answer:

Admitted.

107. The '023 patent states, *inter alia,* at column 8, lines 57-60 that "Dowlex® 2045 also has a distinct peak at an elution temperature of about 98°C., indicating the 'linear' fraction of the whole polymer."

Answer:

Admitted.

108. On information and belief, prior to filing its Complaint in the present action, Dow did not measure "a distinct peak at an elution temperature of about 98°C," as those terms are used in the '023 patent, for any accused NOVA SURPASS® product.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '023 patent." The claims of the patent do not require the measurement of "a distinct peak at an elution temperature of about 98°C." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '023 patent in any NOVA SURPASS® polymer, denied.

109. The '023 patent states, *inter alia,* at column 9, lines 9-12 that "The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)."

Answer:

Admitted.

110. On information and belief, prior to filing its Complaint in the present action, Dow did not identify in any accused NOVA SURPASS® product any interpolymers and/or copolymers that "have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)," as those terms are used in the '023 patent.

Answer:

This paragraph is vague and ambiguous in its statement, "as those terms are used in the '023 patent." The claims of the patent do not require that there be in any accused product any interpolymers and/or copolymers that "have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC)." To the extent this paragraphs seeks an admission that prior to filing the Complaint, Plaintiff did not identify the elements of the invention claimed in the '023 patent in any NOVA SURPASS® polymer, denied.

111. During the prosecution leading to the '023 patent, Dow distinguished its claimed products from blends of multiple homogeneous polymers.

Answer:

Denied.

112. On information and belief, prior to serving its Complaint in the present action, Dow had information that SURPASS® products contain only "homogenously branched" copolymers, as those terms are used in the '023 patent.

Answer:

Denied.

113. On information and belief, Dow served its complaint in this action knowing that NOVA did not infringe the '023 patent.

Answer:

Denied.

114. NOVA has not infringed and is not infringing the '023 patent with its SURPASS® polyethylene products, either directly, contributorily, and/or by inducement.

Answer:

Denied.

115. NOVA is entitled to a declaratory judgment that it has not infringed and is not infringing the '023 patent with its SURPASS® polyethylene products, either directly, contributorily, and/or by inducement.

Answer:

Denied.

COUNTERCLAIM IV: DECLARATORY JUDGMENT OF INVALIDITY OF THE '023 PATENT

116. NOVA adopts and incorporates in this Counterclaim paragraphs 1-6 above, as if set forth herein.

Answer:

Plaintiff's answers for paragraphs 1-6 are incorporated, as if set forth herein.

117. "Example 4" of the '023 patent is directed, *inter alia*, to an "in-situ blend... wherein the homogenously branched substantially linear polymer is made in a first reactor.... [And a] heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor...."

Answer:

Admitted that the quoted language appears in the '023 patent. The phrase "directed, *inter alia*, to" is vague and ambiguous in its usage in this paragraph. To the extent "directed, *inter alia*, to" is intended to mean that "Example 4" discloses an in-situ blend, admitted.

118. The '023 patent does not report a strain hardening coefficient (SHC) value for the blend of "Example 4."

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses a slope of strain hardening coefficient (SHC) value for the blend of "Example 4."

119. The '023 patent does not report an SHC value for any component identified as a component of the blend of "Example 4."

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '023 patent combined with the presumed knowledge of a person

skilled in the art at the time of the effective filing date of the '023 patent discloses a slope of strain hardening coefficient (SHC) value for at least a component identified as a component of the blend of "Example 4."

120. The '023 patent does not report an SHC value for any component identified as a component of an in-situ blend.

Answer:

The term "report" is vague and ambiguous in its usage in this paragraph. To the extent "report" means disclose, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses a slope of strain hardening coefficient (SHC) value for at least a component of an in-situ blend.

121. The '023 patent does not provide conditions to separate an in-situ blend of polymers into components.

Answer:

The phrase "provide conditions" is vague and ambiguous as used in this paragraph. To the extent "provide conditions" means disclose how to identify the components of an in-situ blend of polymers, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses how to identify the components of an in-situ blend of polymers.

122. The '023 patent does not provide conditions to separate an in-situ blend of polymers into separate components where the polymer components have overlapping temperature rising elution fractionation (TREF) elution temperatures.

Answer:

The phrase "provide conditions" is vague and ambiguous as used in this paragraph. To the extent "provide conditions" means disclose how to identify the components of an in-situ blend of

polymers, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses how to identify the components of an in-situ blend of polymers where the polymer components have overlapping temperature rising elution fractionation (TREF) elution temperatures.

123. The '023 patent states, *inter alia*, at column 7, lines 18-19 that "FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening."

Answer:

Admitted.

124. The '023 patent states, *inter alia*, at column 7, lines 38-41 that "FIG. 1 graphically depicts the relationship between the density of the homogeneously branched substantially linear ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient."

Answer:

Admitted.

125. The '023 patent describes "FIG. 1" differently at column 7, lines 18-19 than at column 7, lines 38-41.

Answer:

The term "differently" is vague and ambiguous in its usage in this paragraph. Admitted that the text in the '023 patent at column 7, lines 18-19 is not identical to the text at column 7, lines 38-41.

126. The "FIG. 1" described in the '023 patent at column 7, lines 18-19 is not contained in the '023 patent.

Answer:

Admitted.

127. On information and belief, prior to April 28, 1993, at least one of the named inventors of the '023 patent was aware of a figure as described at column 7, lines 18-19 of the '023 patent.

Answer:

Upon information and belief, denied.

128. On information and belief, prior to April 28, 1993, at least one member of Dow's Patent Department who participated in the prosecution leading to the '023 patent was aware of a figure as described at Column 7, lines 18 - 19 of the '023 patent.

Answer:

Upon information and belief, denied.

129. The figure labeled "FIG. 1" appearing on the fourth page of the issued '023 patent does not depict "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19.

Answer:

The term "depict" is vague and ambiguous in its usage in this paragraph. Admitted that Figure 1 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '023 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

130. The figure labeled "FIG. 2" appearing on the fifth page of the issued '023 patent does not depict "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19.

Answer:

The term "depict" is vague and ambiguous in its usage in this paragraph. Admitted that Figure 2 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '023 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

131. The '023 patent does not contain a figure showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19.

Answer:

Admitted that no figure in the '023 patent expressly illustrates "the various stages of the stress/strain curve used to calculate the slope of strain hardening." Denied that the '023 patent does not disclose "the various stages of the stress/curve used to calculate the slope of strain hardening." The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

132. A figure showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19, is necessary for the understanding of the subject matter claimed in the '023 patent.

Answer:

Denied.

133. The '023 patent states, *inter alia,* at column 7, line 44 that "Table 1 displays the data of FIG. 1 in tabular form:"

Answer:

Admitted.

134. The data contained in Table 1 of the '023 patent corresponds to the data of the "FIG. 1" described in the '023 patent at column 7, lines 38-44 and depicted on the fourth page of the '023 patent.

Answer:

Admitted.

135. The data contained in Table 1 of the '023 patent is not data showing "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19.

Answer:

The term "showing" is vague and ambiguous as used in this paragraph. Admitted that Table 1 does not expressly illustrate "the various stages of the stress/strain curve used to calculate the slope of strain hardening," as described in the '023 patent at column 7, lines 18-19. Denied that the '023 patent does not disclose "the various stages of the stress/strain curve used to calculate the slope of strain hardening." The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses "the various stages of the stress/strain curve used to calculate the slope of strain hardening."

136. Independent Claims 1 and 9 of the '023 patent contain a limitation requiring that component "A" have "a slope of strain hardening coefficient greater than or equal to 1.3."

Answer:

Denied. Under the doctrine of equivalents, claim limitations cover their literal scope and equivalent subject matter.

137. All claims of the '023 patent contain a limitation that component "A" have a "slope of strain hardening coefficient" at least greater than or equal to 1.3.

Answer:

Denied. Under the doctrine of equivalents, claim limitations cover their literal scope and equivalent subject matter.

138. The '023 patent states, *inter alia*, at column 7, lines 22-28 that:
The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

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

where I_2 =melt index in grams/10 minutes.

Answer:

Admitted.

139. The "slope of strain hardening" parameter appearing in the SHC equation defined in the '023 patent at column 7, lines 22-28 is disclosed to be determined using "FIG. 1," wherein "FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined."

Answer:

Denied.

140. A figure showing a "strain hardening region" is not present in the '023 patent.

Answer:

This paragraph is vague in that the phrase "strain hardening region" has no context. To the extent this paragraph seeks an admission that in none of the figures of the '023 patent is there a representation of a polymer with a strain hardening region, denied.

141. The determination of a "parallel line in the strain hardening region" is not disclosed in the '023 patent.

Answer:

Denied.

142. In the prosecution leading to the '023 patent, Dow did not cite any printed publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993 that contains the SHC definition at column 7, lines 22-28 of the '023 patent.

Answer:

Admitted that, upon information and belief, Plaintiff did not cite a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: *(slope of strain hardening)*$(I_2)^{0.25}$* where I_2 =melt index in grams/10 minutes." In all other respects, denied. One or more printed publications cited by Plaintiff and/or the Examiner disclose information defining all parts of the equation as described at column 7, lines 22-28 of the '023 patent.

143. In the prosecution leading to the '023 patent, the Examiners did not cite any printed publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993, that contains the SHC definition at column 7, lines 22-28 of the '023 patent.

Answer:

Admitted that, upon information and belief, the Examiner did not cite a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: *(slope of strain hardening)*$(I_2)^{0.25}$* where I_2 =melt index in grams/10 minutes." In all other respects, denied. One or more printed publications cited by Plaintiff and/or the Examiner discloses information defining all parts of the equation as described at column 7, lines 22-28 of the '023 patent.

144. On information and belief, Dow is not aware of any publication or public use, as those terms are used in 35 U.S.C. § 102, from prior to April 28, 1993, that contains the SHC definition at column 7, lines 22-28 of the '023 patent.

Answer:

Admitted that, upon information and belief, Plaintiff is not aware of a printed publication from prior to April 28, 1993 that expressly states: "The slope of strain hardening coefficient (SHC) is calculated according to the following equation: *(slope of strain hardening)*$(I_2)^{0.25}$* where I_2 =melt index in grams/10 minutes." In all other respects, denied. Plaintiff is aware of one or more printed publications from prior to April 28, 1993 that, singularly or combined, discloses information defining all parts of the equation as described at column 7, lines 22-28 of the '023 patent.

145. The '023 patent indicates that the I_2 parameter in the equation at column 7, lines 22-28 has the units of "grams/10 minutes."

Answer:

Admitted.

146. On information and belief, prior to April 28, 1993, at least one of the named inventors of the '023 patent was aware of units for the "slope of strain hardening" parameter, as that parameter is used in the '023 patent at column 7, lines 22-28.

Answer:

Admitted.

147. The '023 patent does not provide any units for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

Answer:

Admitted that '023 patent does not expressly state specific units to be used for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28. In all other respects,

denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses units to be used for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

148. The '023 patent does not provide any units for the "SHC" parameter in the equation at column 7, lines 22-28.

Answer:

Admitted that '023 patent does not expressly state specific units to be used for the "SHC" parameter in the equation at column 7, lines 22-28. In all other respects, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses units to be used for the "SHC" parameter in the equation at column 7, lines 22-28.

149. In the section of the '023 patent entitled "Determination of the Slope of Strain Hardening Coefficient" beginning at column 6, line 52, the '023 patent refers to both English units (*e.g.*, psi at column 6, line 59) and metric units (*e.g.*, grams/cm^3 at column 7, lines 35-36).

Answer:

Admitted.

150. The '023 patent does not state whether English or metric units should be used for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

Answer:

Admitted that there is no express statement whether English or metric units should be used at column 7, lines 22-28. In all other respects, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses when English or metric units are appropriate for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

151. The '023 patent does not state what units should be used for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

Answer:

Admitted that there is no express statement stating whether specific units for the "slope of strain hardening" parameter should be used in the equation at column 7, lines 22-28. In all other respects, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses what units should be used for the "slope of strain hardening" parameter in the equation at column 7, lines 22-28.

152. The '023 patent incorporates by reference patents that collectively use multiple different units for the slope of a stress/strain curve, including "lbs./in/ /oz./yd.^{2}" in United States Patent No. 3,458,706, "MPa" in United States Patent No. 4,597,920, "KPa" in United States Patent No. 5,059,481, "GPa" and gm/denier" in United States Patent No. 4,413,110, "psi" in United States Patent No. 4,663,220, and "Kpsi" in United States Patent No. 4,865,902.

Answer:

Denied.

153. At column 27, lines 26-29 of U.S. Patent No. 4,413,110, the numerical value reported in units of "GPa" is different from the numerical value reported in "g/d."

Answer:

Admitted that at column 27, lines 26-29 of U.S. Patent No. 4,413,110, that patent states, "[t]he measurement 140 GPa (1587 g/d) . . ." and that the two numerical values "140" and "1587" are different.

154. The numerical value for the SHC parameter in the equation at column 7, lines 22-28 of the '023 patent depends on, *inter alia*, the units used for the "slope of strain hardening" parameter.

Answer:

The paragraph is vague and ambiguous in that no polymer is identified. Plaintiff interprets this paragraph to mean that the value for the SHC parameter for all polymers in all situations in the equation at column 7, lines 22-28 of the '023 patent depends on, *inter alia*, the units used for the "slope of strain hardening" parameter. Under this interpretation, denied.

155. The '023 patent does not specify units for the "slope of strain hardening" parameter.

Answer:

Denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses appropriate units for the "slope of strain hardening" parameter.

156. On November 1, 1999, the patent application leading to Dow's United States Patent No. 6,723,398 B1 ("the '398 patent") was filed in the United States Patent Office.

Answer:

Upon information and belief, admitted.

157. A true and correct copy of the '398 patent is attached hereto as Exhibit i.

Answer:

Upon information and belief, admitted.

158. Pack-Wing S. Chum is a named inventor on both the '398 patent and the '023 patent.

Answer:

Admitted that Pak-Wing S. Chum is a named inventor on both the '398 patent and the '023 patent.

159. On information and belief, Pack-Wing S. Chum was and/or is an employee of Dow.

Answer:

Admitted that Pak-Wing S. Chum was and/or is an employee of Plaintiff.

160. On information and belief, Pack-Wing S. Chum was aware of the contents of the specification of the application leading to the '398 patent at least by January 10, 2000.

Answer:

The term "aware" is vague and ambiguous as used in this paragraph. Admitted that the '398 patent states on its face that a Pak-Wing S. Chum was a named inventor of U.S. Patent No. 6,723,398 B1.

161. Osborne K. McKinney prosecuted both the application leading to the '398 patent and the application leading to the '023 patent.

Answer:

Upon information and belief, admitted.

162. On information and belief, Osborne K. McKinney was and/or is an employee of Dow.

Answer:

Admitted.

163. The "Utility Patent Application Transmittal" dated November 1, 1999, for the application leading to the '398 patent was signed by Osborne K. McKinney.

Answer:

Upon information and belief, admitted.

164. The "Utility Patent Application Transmittal" dated November 1, 1999, for the application leading to the '398 patent was submitted while the application leading to the '023 patent was pending at the United States Patent and Trademark Office.

Answer:

Upon information and belief, admitted.

165. The application leading to the '398 patent was not disclosed by or on behalf Dow in the application leading to the '023 patent.

Answer:

Admitted that application No. 08/927,393, filed on August 27, 1997, did not reference the later filed application No. 09/430,919, filed on November 1, 1999.

166. The application leading to the '398 patent was not cited by the Examiner in the application leading to the '023 patent.

Answer:

Upon information and belief, admitted that the Examiner did not cite application No. 09/430,919, filed on November 1, 1999, in application No. 08/927,393, filed on August 27, 1997.

167. The '398 patent states, *inter alia*, at column 2, lines 45-49 that "FIG. 2 shows the various regions of a typical tensile curve (as load in pounds versus extension in inches) and the particular region used to determine the slope of strain hardening."

Answer:

Admitted.

168. The '398 patent includes on page 4 "FIG. 2," which corresponds to the description in the '398 patent at column 2, lines 45-49.

Answer:

Admitted.

169. "FIG. 2" of the '398 patent shows "various stages of the stress/strain curve used to calculate the slope of strain hardening."

Answer:

This paragraph is vague and ambiguous in that no polymer is specified. Admitted that "FIG. 2" of the '398 patent illustrates various stages of the stress/strain curve used to calculate the slope of strain hardening" for the polymers that are the subject of Figure 2 of the '398 patent. Denied that "FIG. 2" of the '398 patent shows "various stages of the stress/strain curve used to calculate the slope of strain hardening" for all polymers in all situations.

170. As depicted in "FIG. 2" of the '398 patent, the "Strain Hardening Region" begins before the "point of 10% extension before failure."

Answer:

Admitted that for the polymers that are the subject of "FIG. 2" of the '398 patent, the "Strain Hardening Region" may begin before the "point of 10% extension before failure." Denied, however, that all polymers would behave exactly as illustrated in "FIG. 2" of the '398 patent, or that the "Strain Hardening Region" begins before the "point of 10% extension before failure" for all polymers in all situations.

171. The '398 patent discloses that a subsection of the "strain hardening region" is used to determine the "slope of strain hardening."

Answer:

Admitted that for the polymers that are the subject of "FIG. 2" of the '398 patent, the '398 patent discloses that a subsection of the "strain hardening region" can be used to determine the "slope of strain hardening." Otherwise denied that the '398 patent discloses that a subsection of the "strain hardening region" is used to determine the "slope of strain hardening" for all polymers in all situations.

172. The '398 patent states, *inter alia*, at column 11, lines 6-11 that:

> The slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain).

Answer:

Denied.

173. The '023 patent does not disclose that the slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain).

Answer:

Admitted that the '023 patent does not expressly state that "the slope of strain hardening is conveniently taken as a line representing a 10 percent secant tangent which is calculated from the failure point to the point where 10 percent extension before the failure point (where 10 percent extension before is equal to 90 percent of the total extension or strain)." In all other respects, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at

the time of the effective filing date of the '023 patent discloses how to determine the slope of strain hardening.

174. The '398 patent states, *inter alia*, at column 11, lines 12-15 that:

> A more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point.

Answer:

Admitted.

175. The '023 patent does not disclose that a more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point.

Answer:

Admitted that the '023 patent does not expressly state that "a more precise methodology for calculating the slope of strain hardening is performing linear regression analysis using the tensile curve datapoints that represent the last 10 percent extension before the failure point." In all other respects, denied. The '023 patent combined with the presumed knowledge of a person skilled in the art at the time of the effective filing date of the '023 patent discloses how to determine the slope of strain hardening.

176. The '398 patent identifies the "line parallel to the strain hardening region" as a "10 percent secant line."

Answer:

Denied.

177. The '023 patent does not identify the "line parallel to the strain hardening region" as a "10 percent secant line."

Answer:

Admitted.

178. The '023 patent does not identify any subsection of the "strain hardening region" from which the "slope of strain hardening," as those terms are used in the '023 patent, is or should be determined.

Answer:

Denied.

179. No drawing containing the information in "FIG. 2" of the '398 patent related to the region used to determine the "slope of strain hardening" or the units for "slope of strain hardening" is contained in the '023 patent.

Answer:

Admitted that there are no drawings in the '023 patent; there are only computer generated figures.

180. ASTM dimensions for stress/strain curves in accordance with ASTM D-882 are pressure vs. % extension.

Answer:

This paragraph is vague and ambiguous. Pressure vs. % extension is not an expression of "dimensions." The term "ASTM dimensions" is vague and ambiguous as used in this paragraph. Plaintiff consequently lacks information, knowledge, and belief to either admit or deny this averment.

181. The slope of the strain hardening, as depicted in "FIG. 2" in the '398 patent has units of "pounds/inch."

Answer:

Admitted.

182. The '023 patent does not disclose that "slope of strain hardening" should be in units of "pounds/inch."

Answer:

Denied.

183. The units "pounds/inch" do not correspond to the dimensions of pressure vs. % extension.

Answer:

The term "correspond" is vague and ambiguous as used in this paragraph. "Pressure vs. % extension" is not an expression of "dimensions." Denied that "pounds/inch" can never relate to "pressure vs. % extension."

184. Subsequent to the November 1, 1999, filing of the application leading to the '398 patent, Osborne K. McKinney presented arguments on behalf of Dow in the application leading to the '023 patent based on, *inter alia*, values of the "slope of the strain hardening coefficient."

Answer:

Denied.

185. On information and belief, one or more of the named inventors of the '023 patent was aware of the preferred subsection of the "strain hardening region" used to determine the "slope of strain hardening" and/or the units to be used in determining that parameter prior to April 28, 1993.

Answer:

This paragraph assumes a fact that Plaintiff denies, namely that there was a preferred subsection as of April 28, 1993, of the "strain hardening region" for all polymers in all circumstances or situations for use in determining the "slope of strain hardening." Denied.

186. On information and belief, one or more attorneys in Dow's Patent Department who participated in the prosecution leading to the '023 patent was aware of the preferred subsection of the "strain hardening region" used to determine the "slope of strain hardening" and/or units to be used in determining that parameter prior to April 28, 1993.

Answer:

This paragraph assumes a fact that Plaintiff denies, namely that there was a preferred subsection as of April 28, 1993, of the "strain hardening region" for all polymers in all circumstances or situations for use in determining the "slope of strain hardening." Denied.

187. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '023 failed to furnish a drawing necessary for the understanding of the subject matter sought to be patented.

Answer:

Assumes facts that Plaintiff denies: that Plaintiff's '023 failed to furnish a drawing necessary for the understanding of the subject matter sought to be patented. Denied.

188. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '023 patent failed to adequately disclose the SHC parameter recited in each claim of the '023 patent and/or for failed to disclose the best mode for determining SHC because of the omission from the '023 specification of the "FIG. 1" referred to at column 7, lines 22-28.

Answer:

Assumes facts that Plaintiff denies: that the '023 patent failed to disclose the SHC parameter and that the '023 patent failed to disclose the best mode for determining SHC. Denied.

189. On information and belief, at the time Dow served its complaint in this action, Dow knew that the '023 patent failed to disclose units for the "slope of strain hardening" parameter that appears in the SHC equation described at column 7, lines 22-28.

Answer:

Assumes facts that Plaintiff denies: that the '023 patent failed to disclose units for the "slope of strain hardening" parameter that appears in the SHC equation described at column 7, lines 22-28.

Denied.

190. On information and belief, at the time Dow served its Complaint in this action, Dow knew that the use of different units for the "slope of strain hardening" parameter in the equation

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

would result in different SHC values when calculated using this equation.

Answer:

Assumes facts that Plaintiff denies: that different values for SHC would result for all polymers in all circumstances from the use of different units for the "slope of strain hardening" parameter.

Denied.

191. On information and belief, at the time Dow served its complaint in this action, Dow knew that its '023 patent failed to furnish any units for the "slope of strain hardening" parameter that appears in the SHC equation described at column 7, lines 22-28, which units are necessary for calculation of SHC.

Answer:

The use of the term "furnish" in this paragraph is vague and ambiguous. To the extent this paragraph seeks an admission that Plaintiff knew that the units for the slope of strain hardening parameter are not disclosed in the '033 patent, this paragraph assumes a fact that Plaintiff denies.

Denied.

192. The claims of the '023 patent are invalid for failure to comply with the conditions for patentability specified by 35 U.S.C. § 101, *et seq.*, including sections 102, 103, 112, and/or 113.

Answer:

Denied.

RIGHT TO ASSERT ADDITIONAL COUNTERCLAIMS

193. NOVA's investigations into the allegations set forth by in Dow's Complaint are ongoing and discovery has not yet commenced. NOVA expressly reserves the right to assert and pursue additional counterclaims.

Answer:

Admitted that discovery has not yet commenced. Plaintiff is otherwise without sufficient knowledge or information to admit or deny the allegations.

PRAYER FOR RELIEF

For the reasons set forth above, Plaintiff prays for the Court's entry of judgment for it and against NOVA as follows:

Plaintiff incorporates its requested relief in its original Complaint and further requests this Court declare the '053 and '023 patents valid.

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