EXHIBIT E

US005408004A

United States Patent [19]

Lai et al.

[11] Patent Number: 5,408,004

[45] Date of Patent: Apr. 18, 1995

[54] **POLYOLEFIN BLENDS AND THEIR SOLID STATE PROCESSING**

[75] Inventors: **Shih-Yaw Lai**, Sugar Land; **Morris S. Edmondson**, Alvin, both of Tex.

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

[21] Appl. No.: **107,482**

[22] Filed: **Aug. 17, 1993**

[51] **Int. Cl.**[6] **C08L 23/04**; C08L 23/10; C08J 5/00

[52] **U.S. Cl.** **525/240**; 525/198; 264/331.17; 264/322

[58] **Field of Search** 525/198, 240; 264/322, 264/331.7

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,645,992	2/1972	Elston	526/348.6
3,739,052	6/1973	Ayres et al.	
3,947,204	3/1976	Ayres et al.	425/383
3,995,763	12/1976	Ayres et al.	220/74
4,005,967	2/1977	Ayres et al.	425/326
4,014,956	3/1977	Smith et al.	260/853
4,107,243	8/1978	Stearns et al.	264/13
4,115,499	9/1978	Salyer et al.	264/122
4,161,502	7/1979	Wessling et al.	264/119
4,352,766	10/1982	Bradley et al.	264/45.5
4,542,886	9/1985	Yoshimura et al.	264/22
4,607,797	8/1986	Enikolopow et al.	241/23
4,981,760	1/1991	Naito et al.	428/523
5,001,206	3/1991	Bashir et al.	526/352
5,028,633	7/1991	Ohno et al.	514/778
5,028,663	7/1991	Chung	525/198
5,091,133	2/1992	Kobayashi et al.	264/119
5,166,268	11/1992	Ficker	525/198
5,206,075	4/1993	Hodgson	525/240
5,210,142	5/1993	Kale et al.	525/240

FOREIGN PATENT DOCUMENTS

351189	1/1990	European Pat. Off.	C08F 210/16
572034	12/1993	European Pat. Off.	C08F 210/02
590739	4/1994	European Pat. Off.	C08L 23/04
53-75278	7/1978	Japan .	
WO93/13143	7/1993	WIPO	C08F 10/02

OTHER PUBLICATIONS

Schwank—Selected Applications for CGCT Polymers—Sep. 1992, Paper presented at SPO '92.

Pawloski and Raspor, "Articles with Improved Properties Via Solid Phase Forming", Conference Proceedings for the Society of Plastics Engineers, Inc., 43d Annual Technical Conference, Washington, D.C., Apr. 29–May 2, 1985.

Capaccio, et al., "The Drawing Behavior of Linear Polyethylene. I. Rate of Drawing as a Function of Polymer Molecular Weight and Initial Thermal Treatment", J. Polym. Sci., vol. 14, 1641–1658 (1976).

Hidehiko and Kuriyama, "Mechanical Relaxations in γ-Ray-Polymerized Polyethylene", J. Polym. Sci., vol. 14, 1659–1669 (1976).

Cansfield, et al., "The Preparation of Ultra-High Modulus Polypropylene Films and Fibres", Polymer Eng. and Sci., vol. 16, No. 11, 721–724 (1976).

Hope, et al., "Hydrostatic Extrusion of Linear Polyethylene in Tubular and Non-Circular Sections", Poly. Eng. and Sci., vol. 20, No. 8, 540–545, (1980).

Gibson, et al., "Hydrostatic Extrusion of Linear Polyethylene: Effects of Molecular Weight and Product Diameter", J. Poly. Sci., vol. 16, 2015–2030 (1978).

Coffman, "Stretch-forming: a simple process with a lot of potential", Plastics Engineering, 19–21 (Aug., 1977).

Coates, "Hydrostatic Extrusion of Polyoxymethylene", J. Polym. Sci., vol. 16, 2031–2047 (1978).

(List continued on next page.)

Primary Examiner—Carman J. Seccuro, Jr.

[57] **ABSTRACT**

Polyolefin blends characterized by melting and crystallization curves which exhibit either two distinct melt regions, or wherein one component of the blend has a low softening temperature relative to the individual components of the blend, provide an unusually wide window for solid state processing. The solid state processing characteristics of these blends are independent of the manner in which the blends are formulated, e.g. mechanical mixing, solvent dispersion, and the like.

6 Claims, No Drawings

OTHER PUBLICATIONS

Bigg, "A Review of Techniques for Processing Ultra-High Modulus Polymers", Polym. Eng. and Sci., vol. 16, No. 11, 725–734 (1976).

Bigg, et al., "High Modulus Semi-Crystalline Polymers by Solid State Rolling", Polym. Eng. Sci., vol. 22, No. 1, 27–33 (1982).

Krjutchkov, et al., "Solid State Extrusion of Semicrystalline Polymers", Polymer Composites, vol. 7, No. 6, 413–420 (Dec., 1986).

International Search Report, dated Nov. 11, 1994, issued by the EPO acting as the International Searching Authority in PCT/US94/08943.

Ciferri and Ward, Ultra High Modulus Polymers, Applied Science Publ., London (1979).

Krjutchkov, Polymer Composite, vol. 7, #6, pp. 413–420 (1986).

POLYOLEFIN BLENDS AND THEIR SOLID STATE PROCESSING

BACKGROUND OF THE INVENTION

This invention relates to polyolefin blends. In one aspect, the invention relates to polyolefin blends suitable for solid state processing while in another aspect, the invention relates to particular blends of various polyethylenes. In still another aspect, the invention relates to polyolefin blends characterized by melting and crystallization curves exhibiting either two distinct melt regions, or wherein one component has a softening point lower than that of a conventional polyolefin, either technique of which provides an unusually wide window for solid state processing.

While the field of metal forming offers a wide variety of solid state processing, e.g. stamping, forging, rolling, extrusion, etc., the solid state processing of semicrystalline polymers is much more limited. To process a thermoplastic in the solid state, typically the processing temperature is maintained at just a few degrees below the melting point of the polymer. If the processing temperature is above the melting point of the polymer, then the processing is simply a melt extrusion. At temperatures considerably below the melting point of the polymer, the polymer is essentially a solid and its deformation requires a tremendous amount of pressure (often in excess of one million psi). Such enormous pressures make large deformations very difficult, and result in a relatively low production rate and a generally energy inefficient process. Moreover, since the processing temperature is the most critical parameter in solid state processing, this technique has been limited to those polymers and polymer blends with relatively wide (e.g. at least about 20 degrees on the Celsius scale) ranges between their softening and melting temperatures. Since this temperature range is relatively narrow for conventional polyolefins and their blends, these materials have not been the subject of extensive, commercial-scale solid state processing.

Despite their relatively narrow processing temperature window, the sheer commercial scale of the polyolefin market has generated considerable interest in applying this technique to polyolefins. The potential benefits to be gained include energy efficiency, speed, and scrap reduction. Ciferri and Ward in "Ultra High Modulus Polymers", *Applied Science Publications*, London (1979), teach that the extrusion of polymers below the melting point is a promising method of producing highly oriented materials. Krjutchkov, et al. in *Polymer Composite*, Vol. 7, No. 6, pp. 4-13-420 (1986), disclosed the detailed investigations of the dynamics of solid state extrusion, and they have also postulated a model to correlate the flow of instability in extrudate defects to the extrusion temperature and pressure.

Chung in U.S. Pat. No. 5,028,663 teaches that certain blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) prepared by solution mixing can achieve a broader operating window for certain solid state processing applications than would otherwise be achieved by mechanical mixing. The melting peak of each component in the blend is separated due to solution precipitation such that large deformation processing can be performed at a temperature between the melting peaks of the two components.

Pawloski, et al. in U.S. Pat. Nos. 4,352,766, 4,161,502 and 3,739,052 teach a unique process called Solid Phase Forming (SPF) to form polymers and composites at a pre-melt state. This unique fabrication process induces a biaxial orientation throughout the finished parts.

Enikolopow, et al. in U.S. Pat. No. 4,607,797 teach a process called Solid State Sheer Extrusion or Pulverization to perform polymer extrusion at a temperature below the peak melting temperature of the polymer. However, Shutov has observed in a 1992 I.I.T. Research Report that certain polymers, such as HDPE, polypropylene (PP) and polycarbonate (PC) did not perform well in this process.

The disclosures of each of the patents referenced above are incorporated herein by reference.

SUMMARY OF THE INVENTION

According to this invention, polyolefin blends characterized by melting and crystallization curves which exhibit either two distinct melt regions, or a low softening point relative to the high melting component of the blend, provide an unusually wide window for solid state processing. These blends comprise at least 10 percent by weight of the low melting component, and the difference between the peak melting temperature of the low melting component and the high melting component is at least about twenty degrees on the Celsius scale. These blends are processed in their solid state at a temperature above about the peak melting temperature of the low melting component and below the peak melting temperature of the high melting component. The solid state processing characteristics of the blends of this invention are independent of the manner in which the components are mixed, e.g. mechanical, solvent, etc.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyolefin blends of this invention comprise two or more, typically two, polyolefin components. These blends are characterized by having a solid state processing temperature (Tp) defined by

$$T_{m1} < T_p < T_{m2}$$

in which the T_{m2} is the peak melting temperature of the high melting component, and T_{m1} is the peak melting temperature of the low melting component. Typically, the difference or range between T_{m2} and T_{m1}, i.e. $T_{m2} - T_{m1}$, is greater than about twenty, preferably greater than about thirty, and most preferably greater than about forty, degrees on the Celsius scale.

The components of the blends of this invention are polyolefins, e.g. polyethylenes, polypropylenes, dienes, styrene, etc. Preferred polyolefins are the various polyethylenes and polypropylenes, and preferred blends are those containing at least one polyethylene, particularly a substantially linear ethylene polymer.

The polyethylenes can be divided into two broad classes, heterogeneously branched and homogeneously branched. The heterogeneously branched polyethylenes that can be used in the practice of this invention fall into two broad categories, those prepared with a free radical initiator at high temperature and high pressure, and those prepared with a coordination catalyst at high temperature and relatively low pressure. The former are generally known as low density polyethylenes (LDPE) and are characterized by branched chains of polymerized monomer units pendant from the polymer backbone. LDPE polymers generally have a density

between about 0.910 and 0.935 grams per cubic centimeter (g/cc).

Ethylene polymers and copolymers prepared by the use of a coordination catalyst, such as a Ziegler or Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone. High density polyethylene (HDPE), generally having a density of about 0.941 to about 0.965 g/cc, is typically a homopolymer of ethylene, and it contains relatively few branch chains relative to the various linear copolymers of ethylene and an α-olefin. HDPE is well known, commercially available in various grades, and is useful in this invention.

Linear copolymers of ethylene and at least one α-olefin of 3 to 12 carbon atoms, preferably of 4 to 8 carbon atoms, are also well known, commercially available and useful in this invention. As is well known in the art, the density of a linear ethylene/α-olefin copolymer is a function of both the length of the α-olefin and the amount of such monomer in the copolymer relative to the amount of ethylene, the greater the length of the α-olefin and the greater the amount of α-olefin present, the lower the density of the copolymer. Linear low density polyethylene (LLDPE) is typically a copolymer of ethylene and an α-olefin of 3 to 12 carbon atoms, preferably 4 to 8 carbon atoms (e.g., 1-butene, 1-octene, etc.), that has sufficient α-olefin content to reduce the density of the copolymer to that of LDPE. When the copolymer contains even more α-olefin, the density will drop below about 0.91 g/cc and these copolymers are known as ultra low density polyethylene (ULDPE) or very low density polyethylene (VLDPE). The densities of these linear polymers generally range from about 0.87 to 0.91 g/cc.

Both the materials made by the free radical catalysts and by the coordination catalysts are well known in the art, as are their methods of preparation. Relevant discussions of both of these classes of materials, and their methods of preparation, are found in U.S. Pat. No. 4,950,541 and the patents to which it refers, all of which are incorporated herein by reference.

The homogeneously branched polyethylenes that can be used in the practice of this invention also fall into two broad categories, the linear homogeneously branched and the substantially linear homogeneously branched. Both are known. The former and their method of preparation are described in U.S. Pat. No. 3,645,992 to Elston, and the latter and their method of preparation are fully described in U.S. Pat. Nos. 5,272,236 and 5,278,272, all of which are incorporated into and made a part of this application by reference. Examples of the former are the Tafmer TM polymer of Mitsui and the Exact TM polymer of Exxon, while an example of the latter are the polymers made by the Insite TM Technology of The Dow Chemical Company.

As here used, "substantially linear" means that the polymer backbone is substituted with about 0.01 long-chain branches/1000 carbons to about 3 long-chain branches/1000 carbons, preferably from about 0.01 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons, and more preferably from about 0.05 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons. In contrast, simply "linear" means that long chain branching is essentially absent from the polymer backbone. Long-chain branching is here defined as a chain length of at least about 6 carbon atoms, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long-chain branch can be about the same length as the length of the polymer backbone.

These unique substantially linear homogeneously branched polymers (subsequently referred to as "substantially linear ethylene polymers") are prepared by using constrained geometry catalysts (CGC), and are characterized by a narrow molecular weight distribution and if an interpolymer, by a narrow comonomer distribution. As here used, "interpolymer" means a polymer of two or more comonomers, e.g. a copolymer, terpolymer, etc. Other basic characteristics of these substantially linear ethylene polymers include a low residuals content (i.e. low concentrations in the substantially linear ethylene polymer of the catalyst used to prepare the polymer, unreacted comonomers, if any, and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability even though the molecular weight distribution is narrow relative to conventional olefin polymers.

While the substantially linear ethylene polymers used in the practice of this invention include substantially linear ethylene homopolymers, preferably these substantially linear ethylene polymers comprise between about 95 and 50 wt % ethylene, and about 5 and 50 wt % of at least one α-olefin comonomer, more preferably 10 to 25 wt % of at least one α-olefin comonomer. Percent comonomer is measured by Infrared Spectroscopy according to ASTM D-2238 Method B. Typically, the substantially linear ethylene polymers are copolymers of ethylene and an α-olefin of 3 to about 20 carbon atoms (e.g. propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, styrene, etc.), with a density of 0.850 to about 0.960 grams per cubic centimeter (g/cm^3), preferably of 0.870 to about 0.910 g/cm^3. The melt flow ratio, measured as I_{10}/I_2 (ASTM D-1238), is greater than or equal to 5.63, and is preferably from about 6.5 to 15, more preferably from about 7 to 10. The molecular weight distribution (M_w/M_n), measured by gel permeation chromatography (GPC), is defined by the equation:

$$M_wM_n \leq (I_{10}/I_2) - 4.63,$$

and is preferably between about 1.5 and 2.5. For the substantially linear ethylene polymers, the I_{10}/I_2 ratio indicates the degree of long-chain branching, i.e. the larger the I_{10}/I_2 ratio, the more long-chain branching in the polymer.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R. N. Shroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, No. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97–99, both publications of which are incorporated herein by reference. GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 250 to 5500 psig using about a 7.54 cm diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/CM^2. These substantially linear ethylene interpolymers and homopolymers preferably have a PI in the range of about 0.01 kpoise to about 50

kpoise, preferably about 15 kpoise or less, which is less than or equal to about 70% of the PI of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S. Pat. No. 3,645,992) at about the same I_2 and M_w/M_n.

An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in the *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 film gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40× magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers and homopolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S. Pat. No. 3,645,992) having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown films and bags therefrom), surface defects should be minimal, if not absent, for good film quality and properties. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers and homopolymers used in making the biaxially oriented, heat-shrinkable film of the present invention is greater than about 4×10^6 dynes/cm^2. The critical shear rate at the onset of surface melt fracture (OSMF) and the onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

As here used, "homogeneously branched" means that the comonomer is randomly distributed within a given molecule and that substantially all of the copolymer molecules have the same ethylene/comonomer ratio. The distribution or homogeneity of comonomer branches for the substantially linear ethylene interpolymers and homopolymers is characterized by its SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index), and it is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, by Wild et al., *Journal of Polymer Science, Poly. Phys, Ed.*, Vol. 20, p. 441 (1982), or in U.S. Pat. No. 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the substantially linear homogeneously branched interpolymers and homopolymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

Both the linear homogeneously branched and the substantially linear homogeneously branched ethylene polymers used in this invention have a single melting peak, as measured using differential scanning calorimetry (DSC), in contrast to heterogeneously branched linear ethylene polymers, which have two or more melting peaks due to their broad branching distribution.

The unique characteristic of the homogeneously branched, substantially linear ethylene polymers is a highly unexpected flow property where the I_{10}/I_2 value of the polymer is essentially independent of the polydispersity index (i.e., M_w/M_n) of the polymer. This is contrasted with conventional linear homogeneously branched and linear heterogeneously branched polyethylene resins having rheological properties such that to increase the I_{10}/I_2 value the polydispersity index must also be increased.

The preferred melt index, measured as I_2 (ASTM D-1238, condition 190/2.16 (formerly condition E)), is from about 0.5 g/10 min to 20 g/10 min, more preferably 1 to 5 g/10 min. Typically, the preferred substantially linear ethylene polymers used in the construction of the plastic films used in this practice of this invention are homogeneously branched and do not have any measurable high density fraction, (i.e. short chain branching distribution as measured by Temperature Rising Elution Fractionation which is described in U.S. Pat. No. 5,089,321, and which is incorporated into and made a part of this application by reference), e.g. they do not contain any polymer fraction that has a degree of branching less than or equal to 2 methyl/1000 carbons. These preferred substantially linear ethylene polymers have a single differential scanning calorimetry (DSC) melting peak.

The polypropylene component of this invention, if present, is a homopolymer or one or more copolymers of propylene and up to about 20 mole percent ethylene or other α-olefin having up to about 12 carbon atoms. If a copolymer, it can be random, block or graft. The polypropylene component of this has a typical melt flow rate (as determined by ASTM D-1238, Condition 230/2.16 (formerly Condition L)) of between about 0.1 and 30, and preferably between about 0.8 and 30.

The blends of this invention can also include polyolefins derived from post-consumer recycle (PCR) sources. These materials will vary in composition, but include HDPE derived from milk bottle recycled resin and LLDPE derived from recycled grocery sacks. The PCR resins used in this invention usually have a polyethylene content of at least about 70 wt %, based on the weight of the resin, up to about 100 wt %. The polyethylenes in the PCR resins usually have a melt index between about 0.1 and about 10, and a density between about 0.86 and about 0.97 g/cm^3.

Typically, the polyolefin blends of this invention comprise at least about 10 percent, preferably at least about 20 percent and more preferably at least about 30 percent, based on the weight of the blend, of the low melting component. In a preferred embodiment of this invention, the component with the low melting or softening temperature is at least one linear or substantially linear homogeneously branched polyethylene, e.g. at least one of a Tafmer TM , Exact TM or a polymer made by Insite TM Technology, or an ethylene-propylene rubber, or an ethylene-propylene-diene monomer terpolymer. More preferably, the low melting temperature component of the blend is a substantially linear homogeneously branched polymer, e.g. a polymer made by Insite TM . In these embodiments, the remainder of the

blend comprises one or more, preferably one, heterogeneously branched polyethylene.

The solid state processing temperature of these blends is usually at least about 5, and preferably at least about 10, degrees on the Celsius scale below the peak melting temperature of the blend component with the highest melting temperature, and it is usually at least about 5, preferably at least about 10, degrees on the Celsius scale above the melting or softening temperature of the blend component with the lowest melting or softening temperature.

The polyolefin blends of this invention can be prepared by any one of a number of different methods that ensures a relatively homogenous blend, the particular method employed being a matter of convenience. Illustrative methods include roller milling, extrusion, solvent mixing, and the like. Similarly, the blends can be processed by any conventional solid state technique, e.g. stamping, forging, rolling, extrusion, etc.

The following examples are illustrative of certain specific embodiments of this invention. All parts and percentages are by weight unless otherwise noted.

SPECIFIC EMBODIMENTS

EXAMPLE 1

Sample E-1 is prepared from a 50/50 blend of CGC resin (Sample C-1) and HDPE resin (Sample C-2) using a Haake blender operated for 4 minutes at 180° C. Sample C-5 is prepared in the same manner except that it is prepared from a 50/50 blend of conventional LLDPEs (Samples C-3 and C-4). All the samples except Sample C-1 are subjected to solid state extrusion evaluation by using an Instron Capillary Rheometer (ICR) at 105° C. using a Number 8 die (0.0494 inches in diameter, length/diameter ratio of 5.10). Sample E-1 (with a T_p of 50 (133-83)) is successfully extruded at a plunger speed of 0.1 inch per minute and at a pressure of 250 psi. The other samples (including Sample C-5 with a T_p of 10 (122-132)) can not be extruded at these conditions, or even at the maximum safe extrusion pressure of the ICR of 4500 psi. These results are reported in Table I.

TABLE I

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	Solid State Extrudable
E-1	CGC/HDPE*	1.33	0.926	—	Yes
C-1	CGC	1.33	0.893	83	NA±
C-2	HDPE	1.0	0.959	133	No
C-3	LLD-3	1.0	0.920	122	No
C-4	LLD-4	2.0	0.930	122	No
C-5	LLD-3/LLD-4*	1.4	0.925	—	No

*50/50/Blend based on weight.
±NA = Not applicable: above melting point

EXAMPLE 2

The procedures of Example 1 are repeated with different samples (although the composition of Sample C-6 is the same as the composition of Sample C-1). Samples E-2 (a blend of C-6 and C-7) (with a T_p of 51) and E-3 (a blend of C-8 and C-9) (with a T_p of 79) are successfully extruded on the ICR at a plunger speed of 0.1 inch per minute, a pressure of about 2800 psi, a temperature of about 105° C., and using a Number 2 die (0.030 inch, length/diameter ratio of 33.3). Neither the Tafmer TM A-4085 resin nor the polypropylene resin could be extruded at these conditions, or even at the maximum safe extrusion pressure of 4500 psi. The results are reported in Table II.

TABLE II

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	Solid State Extrudable
E-2	CGC/HDPE*	2.33	0.926	—	Yes
C-6	CGC	1.78	0.893	83	NA***
C-7	HDPE	10.	0.962	134	NM±
E-3	Tafmer TM /PP**	1.4	0.925	—	Yes
C-8	Tafmer TM A-4085	1.0	0.88	88	No
C-9	PP	35.0	—	167	No

*50/50 Blend based on weight.
**30/70 Blend based on weight.
±NM = Not measured.
***NA = Not applicable: above melting point

EXAMPLE 3

The procedures of Example 1 are repeated with different samples. The compositions of Samples C-10 and C-12 are the same. The PCR resin of Sample C-13 is post-consumer recycled grocery sack resin from Advanced Environmental Recycling Technology of Little Rock, Ark., and the PCR resin of Sample C-11 is post-consumer recycled milk bottle resin FR-120 flake from Akron WTE Corp of Akron, Ohio. Both the resins of Samples E-4 (a blend of C-10 and C-11) and E-5 (a blend of C-12 and C-13) (with a T_p of 49) were successfully extruded under the same conditions as those used in Example 2. Neither the resin of C-11 nor the resin of C-13 are extruded under these conditions, and they cannot be extruded under these conditions even at the maximum safe extrusion pressure of 4500 psi. The results are reported in Table III.

TABLE III

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	Solid State Extrudable
E-4	CGC/PCR*	—	0.912	—	Yes
C-10	CGC	1.0	0.882	86	NA**

TABLE III-continued

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	Solid State Extrudable
C-11	PCR	0.75	0.955	132	No
E-5	CGC/PCR*	1.4	0.935	—	Yes
C-12	CGC	1.0	0.882	86	NA**
C-13	PCR	0.4	0.962	135	No

*30/70 Blend based on weight.
**NA — Not applicable: above melting point.

EXAMPLE 4

The procedures of Example 1 are repeated with different samples. Sample C-14 (which is the same as Sample C-3) is a conventional LLDPE with a similar melt index and density as Sample E-6 (a blend of C-16 and C-15) (with a T_p of 107). Both Samples E-6 and C-14 are compression molded into a 125 mil thick plaque according to the procedures of ASTM-1238. The plaques are heated to 65° C., and then compressed in a 40 ton (2075 psi) solid phase forming machine for 3 minutes. The samples are then cooled under the same pressure, removed at room temperature, and the modulus and percent deformation determined. These results are reported in Table IV, and the modulus and percent deformation characteristics of Sample E-6 are clearly superior to those of Sample C-14.

TABLE IV

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	% Modulus Deformed	% Modulus (psi)
E-6	HDPE/LD*	1.01	0.922	—	203	39,900
C-14.	LLD-3	1.0	0.920	122	162	16,120
C-15	LD	1.01	0.856	26	NM±	NM±
C-16	HDPE	1.0	0.959	133	NM±	NM±

*35/65 Blend based on weight.
± NM = Not measured.

Although the invention has been described in considerable detail through the preceding examples, this detail is for illustration purposes only, and it is not to be construed as a limitation on the spirit and scope of the invention as described in the following claims.

What is claimed is:

1. A process for shaping a solid polyolefin blend, the process comprising the steps of:

A. Heating a solid polyolefin blend which comprises at least a first and second polyolefin, the first of which is a substantially linear homogeneously branched polyethylene characterized as having:

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

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

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

c) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2, with a softening temperature of at least about 10 degrees on the Celsius scale lower than the softening temperature of the second polyolefin, the first polyolefin comprising at least about 10 percent of the total weight of the polyolefin blend, the polyefin blend heated to a processing temperature above the softening temperature of the first polyolefin but below the softening temperature of the second polyolefin;

B. Shaping the blend at the processing temperature; and

C. Cooling the shaped blend of (B) to a temperature below the processing temperature.

2. The process of claim 1 in which the second polyolefin is at least one of high density polyethylene, low density polyethylene, linear low density polyethylene, and ultra low density polyethylene.

3. The process of claim 2 in which the first polyolefin comprises at least about 20 percent of the total weight of the polyolefin blend.

4. The process of claim 3 in which the process temperature is a temperature of at least about 5 degrees on the Celsius scale lower than the softening temperature of the first polyolefin, and at least about 5 degrees on the Celsius scale higher than the softening temperature of the second polyolefin.

5. The process of claim 3 in which the processing temperature is at least about 10 degrees on the Celsius scale lower than the softening temperature of the second polyolefin, and at least about 10 degrees higher than the softening temperature of the first polyolefin.

6. The process of claim 5 in which the polyolefin blend is prepared by mechanically mixing the first and second polyolefins with one another.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,408,004
DATED : April 18, 1995
INVENTOR(S) : Lai et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 44, "$M_wM_n \leqq (I_{10}/I_2)$- 4.63" should be replaced by -- $M_w/M_n \leqq (I_{10}/I_2)$- 4.63 --.

Column 5, line 60, "*phys,*" should be replaced by -- *phys.* --.

Claim 4, line 4, "first" should be replaced by -- second --.

Claim 4, line 6, "second" should be replaced by -- first --.

Signed and Sealed this

Fifteenth Day of April, 1997

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

EXHIBIT F

ISSUE CLASSIFICATION	Class	Subclass
	528	348

08/054379



ABANDONED

UTILITY SERIAL NUMBER	PATENT DATE	PATENT NUMBER
08/054379		

SERIAL NUMBER	FILING DATE	CLASS	SUBCLASS	GROUP ART UNIT	EXAMINER
08/054,379	04/28/93	528	348.3	~~1502~~ 1505	Wu

PAK-WING STEVE CHUM, LAKE JACKSON, TX; GEORGE W. KNIGHT, LAKE JACKSON, TX; RONALD P. MARKOVICH, FRIENDSWOOD, TX; SHIH-YAW LAI, SUGAR LAND, TX.

CONTINUING DATA********
VERIFIED THIS APPLN IS A CIP OF 07/776,130 10/15/91
Yes DW

Wu 1505
528/348.3

FOREIGN/PCT APPLICATIONS********
VERIFIED
None DW

FOREIGN FILING LICENSE GRANTED 08/26/93

70098

sign priority claimed	USC 119 conditions met	filed and Acknowledged	AS FILED	STATE OR COUNTRY	SHEETS DRWGS.	TOTAL CLAIMS	INDEP. CLAIMS	FILING FEE RECEIVED	ATTORNEY'S DOCKET NO.
☐ yes ☒ no	☐ yes ☒ no	Examiner's Initials DW	→	TX	2	30	4	$1,134.00	C40121G

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
BLDG. B-1211
DALLAS, TX 77541

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

U.S. DEPT. of COMM./Pat. & TM Office — PTO-436L (rev. 10-78)

PARTS OF APPLICATION FILED SEPARATELY

Applications Examiner

NOTICE OF ALLOWANCE MAILED

Assistant Examiner

CLAIMS ALLOWED

Total Claims	Print Claim

ISSUE FEE

Amount Due	Date Paid

DRAWING

Sheets Drwg.	Figs. Drwg.	Print Fig.

Label Area

Primary Examiner

PREPARED FOR ISSUE

ISSUE BATCH NUMBER

WARNING: The information disclosed herein may be restricted. Unauthorized disclosure may be prohibited by the United States Code Title 35, Sections 122, 181 and 368. Possession outside the U.S. Patent & Trademark Office is restricted to authorized employees and contractors only.

PTO-436A
(/92)

08/054379

[redacted]

APPROVED FOR LICENSE

INITIALS

Date Entered or Counted

ABANDONED

CONTENTS

Date Received or Mailed

RECEIVED GROUP 160

SEP 0 2 1993

1.	Application ____ papers.	
2.	LTR. Req. Signatures	6-19-93
3.	Decl & Discharge	7-13-93
4.	Rej. (3 Mons.)	11-15-93 11/12
5.	Ext of time (3mo)	May 18, 1994 5/13
6.	Certificate of Mailed	May 18, 1994
7.	3. Rej 3 mos.	2/27/94 2/27
8.	Ext of time (3mo)	Jan 27, 1995
9.	Notice of abandonment	3/6/95 3/6
10.		
11.		
12.		
13.		
14.		
15.		
16.		
17.		
18.		
19.		
20.		
21.		
22.		
23.		
24.		
25.		
26.		
27.		
28.		
29.		
30.		
31.		
32.		

MAIL ROOM
MAY
13
1994
PAT. & TRADEMARK OFF.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Pak-Wing Steve Chum et al.

Serial No.: 08/054,379

Filed: April 28, 1993

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

Docket No.: C-40,121-G

Group Art Unit: 1505

Examiner: D. Wu

RECEIVED
JUN 0 1 1994
GROUP 150

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, on May 13, 1994
DATE OF DEPOSIT

Jan Alverson
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Jan Alverson
SIGNATURE OF PERSON SIGNING CERTIFICATE

5-13-94
DATE OF SIGNATURE

Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

RESPONSE A

In response to the Office Action dated November 15, 1993, Applicants have enclosed a request for a three (3) month extension of time, thereby extending the period of response to May 15, 1994. In addition, Applicants respectfully request entry of the following amendments and reconsideration in view of the following remarks:

In the Specification:

Page 1, line 3, after the words "number 07/776,130," please insert the words -- now USP 5,272,236, -- ;

p. 1, line 4, after the words "number 07/939,281," please insert the words -- now USP 5,278,272, -- ;

p. 3, line 2, please delete the word "temperture" and insert therefore the word -- temperature --;

p. 3, line 14, please the letters "e.g," and insert therefore the letters -- e.g., --;

p. 3, line 15, after the words "The compositions comprise" please insert the letter -- (A) --;

p. 3, line 17, please delete the symbol " : ";

p. 3, line 18, please delete the letter "(A)";

p. 5, line 9, please delete the word "homogeniety" and insert therefore the word -- homogeneity --;

p. 5, line 28, please delete the word "homogeneouslt" and insert therefore the word -- homogeneously --;

p. 8, line 4, please delete the word "substantialy" and insert therefore the word -- substantially --;

p. 10, lines 11 and 16, please delete the word "intial" and insert therefore the word -- initial --;

p. 11, line 2, please delete the word "heterogenously" and insert therefore the word -- heterogeneously --;

p. 14, line 5, please delete the word "tempertaures" and insert therefore the word -- temperatures --;

p. 14, line 9, please delete the word "concommitantly" and insert therefore the word -- concomitantly --;

p. 17, line 23, please delete the word "decribed" and insert therefore the word -- described --;

p. 17, line 27, please delete the word "dicusses" and insert therefore the word -- discusses --;

p. 18, line 11, please delete the word "terepthalate" and insert therefore the word -- terephthalate --;

p. 22, line 5, please delete the word "coplymer" and insert therefore the word -- copolymer --;

p. 22, line 10, please delete the word "recator" and insert therefore the word -- reactor --;

p. 23, line 4, please delete the word "baout" and insert therefore the word -- about --;

p. 23, line 5, please delete the word "distrubution" and insert therefore the word -- distribution --;

p. 26, line 11, please delete the word "ipact" and insert therefore the word -- impact --;

p. 26, line 12, please delete the words "DC ppt tear" and insert therefore the words -- CD ppt tear --.

In the Claims:

Please cancel Claims 9-16 and 24-30 without prejudice.

Please amend the following claims:

1. (Amended) 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[:]

[(A)] 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) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and wherein the heterogeneously branched ethylene polymer has no more than about

10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to about 1.3.

2. (Amended) The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3.

---

17. (Amended) In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

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

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

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

(iv) no linear polymer fraction, and

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

wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient greater than or equal to about 1.3.

18. (Amended) The improvement of claim 17 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3.

REMARKS

The amendments to the specification update the priority application data and correct obvious typographical spelling errors. Applicants regret the errors and respectfully request that the amendments to the specification be entered.

The amendments to independent Claims 1 and 17 describing the heterogeneously branched ethylene polymer are supported in the specification on p. 14, lines 22-23. The other amendment to independent Claim 1 clarifies the composition used to make the film as comprising components (A) and (B). The amendments to dependent Claims 2 and 18 are supported in Table 1, p. 12, in Polymer Q. These amendments do not add new matter. Entry of the amendments is respectfully requested.

Applicants also affirm the election of Group I, Claims 1-8 and 17-23. Applicants reserve the right to timely file divisional applications to the non-elected subject matter of Group II (Claims 9-16 and 24-30).

THE REJECTIONS

1. Claims 1-8 and 17-23 are rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter. Specifically, the language "substantially linear ethylene/alpha-olefin interpolymer" in claims 1 and 17 is allegedly in conflict with language "no linear polymer fraction."

2. Claims 2 and 18 are rejected under 35 USC 112, first paragraph, as the disclosure is allegedly enabling only for claims limiting the slope of strain hardening coefficient up to 2.265.

3. Claims 1-8 and 17-23 are rejected under 35 USC 102(b) as anticipated by, or in the alternative, under 35 USC 103 as obvious over, WO 90/03414 (WO '414).

4. Claims 1-8 and 17-23 are rejected under 35 USC 103 as being unpatentable over USP 5,206,075 (Hodgson).

APPLICANTS' RESPONSE

Applicants discovered that films made from specific ethylene polymer compositions have enhanced properties. The ethylene polymer compositions comprise at least one substantially linear ethylene polymer and at least one heterogeneously branched ethylene polymer. The substantially linear ethylene polymer is not a linear polymer, but has long chain branching and an absence of a linear polymer fraction. The substantially linear ethylene polymers used herein are homogeneous polymers having a narrow molecular weight distribution (MWD) and a narrow or uniform composition distribution (CD). The narrow MWD (generally, MWD ≈ 2) means that the length of the polymer chains is relatively uniform, and the narrow CD means that each polymer chain contains a relatively uniform amount (e.g. weight percent) of α-olefin in copolymerized form and randomly dispersed along the polymer backbone and along any long chain branches. The substantially linear ethylene polymer also has a uniform (i.e., homogeneous) short chain branching distribution, meaning that essentially each polymer molecule has the same number of short chain branches along the polymer chain. In contrast, the heterogeneously branched ethylene polymers, by definition, have broader MWD's, broader CD and different amounts of short chain branching. The heterogeneously branched ethylene polymers are typically prepared using Ziegler catalysis. As Figure 1 demonstrates, each of the polymer components used in Applicants' invention has different branching distributions. The novel films which Applicants have discovered have improved impact and tensile properties and an especially good combination of modulus, yield, ultimate tensile and toughness. See, for example, p. 3, lines 9-14 of the specification and Table 3 (p. 25) and the summary discussion on p. 26.

1. Applicants respectfully submit that the basis of rejection of Claims 1-8 and 17-23 under 35 U.S.C. § 112, second paragraph, is in error. Applicants have taught and claimed that the substantially linear ethylene polymer has long chain branching and that such a substantially linear ethylene polymer has no measurable linear polymer fraction (i.e., no high density fraction) as measured by temperature

rising elution fractionation. See the teaching, for example, at p. 5, lines 23-32 in the Specification. This "high density fraction" or linear polymer fraction is lacking from the substantially linear ethylene polymers used in Applicants' invention. Applicants have taught that conventional ethylene polymers (i.e., LLDPE made using Ziegler catalysis) comprise a variety of polymer molecule components, some molecules having numerous short chain branches and some having no short chain branches. The short chain branches are the result of uneven comonomer incorporation during polymerization, which results in a polymer product having several different types of polymer molecules. For example, see the discussion at p. 13, line 7 through p. 14, line 10. Figure 2 also graphically depicts the relative amounts of the short chain branching contained in a conventional Ziegler polymerized polyethylene polymer (Dowlex™ 2045, a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company). Note how the ATREF curve is much broader over the elution temperature range for the Dowlex™ 2045 polymer, as compared to the homogeneously branched substantially linear ethylene polymers. Applicants respectfully believe that there is no confusion by using the terms "substantially linear ethylene/alpha-olefin interpolymer" and "no linear polymer fraction" to describe the properties of the substantially linear ethylene polymer, since such terms are not contradictory, but rather complimentary. Accordingly, Applicants respectfully traverse the rejection of claims 1-8 and 17-23 under 35 U.S.C. § 112, second paragraph as being indefinite.

2. Applicants have listed substantially linear ethylene polymers with their respective slope of strain hardening coefficients in Table 1. The data of Table 1 is also plotted in Figure 1. Applicants have shown that a substantially linear ethylene polymer having a density of about 0.9216 g/cm^3 has a slope of strain hardening coefficient (SHC) of about 2.3 (see Polymer Q of Table 1). Applicants have amended dependent claims 2 and 18 to incorporate this upper limit for SHC and respectfully traverse the rejection of claims 2 and 18, as amended, under 35 USC 112, first paragraph.

3. WO '414 discloses blends of ethylene interpolymer components with narrow molecular weight and composition

distributions. Each component of WO '414 has a M_w/M_n value less than or equal to 3 and a composition distribution breadth index (CBDI) of 50% or higher. Furthermore, the blend components are each linear. See page 6, line 14, 7, line 28, and page 12, line 33, among others. In contrast to WO '414, Applicants' film is made from ethylene polymer compositions which comprise at least one substantially linear ethylene polymer and at least one heterogeneously branched ethylene polymer (i.e., a conventional LLDPE, as WO '414 describes such heterogeneously branched ethylene polymers). The substantially linear ethylene polymer used in Applicants' invention is not a linear polymer, but instead is an ethylene polymer having long chain branching. The substantially linear ethylene polymers used in Applicants' invention are patentably distinct from the linear ethylene polymers used in WO '414 (see USP 5,272,236 and USP 5,278,272). In addition, the heterogeneously branched ethylene polymer used as the other component of the ethylene polymer compositions used to make the novel film has a broad short chain branching distribution, as Figure 2 demonstrates. WO '414 specifically calls for their blends to each have a CBDI of at least 50%. Consequently, both components of the film of Applicants' ethylene polymer compositions are different from the homogeneously branched linear ethylene polymers used in the blends of WO '414.

WO '414 neither teaches nor suggests the use of a substantially linear ethylene polymer in combination with a heterogeneously branched ethylene polymer. However, WO '414 does lead one skilled in the art away from the use of conventional heterogeneously branched ethylene polymers in their blends. For example, WO '414 states: "The higher molecular weight fraction containing relatively less comonomer as on conventional LLDPE may cause an anisotropic morphology during fabrication processing known as 'row nucleated' or 'shish-ka-bob' morphology. *This anisotropic morphology is believed to contribute to poor toughness in articles crystallized from flowing melts.*" (Page 11, lines 14-20, emphasis added in italics.).

Thus, in direct contrast to that discovered by Applicants, WO '414 concludes that blends of a homogeneously branched ethylene polymer with conventional LLDPE results in thermally formed articles having

poor toughness. Applicants have shown in Table 3 that Examples 1 and 2 both have significantly higher dart impact than comparative example 3. Examples 1 and 2 also have higher machine and cross direction toughness than comparative example 3.

WO '414 specifically describe their polymer components as linear and as having CBDI greater than 50%, and also teach against using conventional (i.e., Ziegler polymerized heterogeneously branched) LLDPE. See also Figure 2 of WO '414, showing the broad CBDI of a "typical prior art LLDPE." (p. 5, lines 28-30 and Figure 2 of WO '414). Accordingly, WO '414 neither anticipates nor obviates Applicants' claimed invention of film made from an ethylene polymer composition comprising at least one substantially linear ethylene polymer and at least one heterogeneously branched ethylene polymer. Thus, Applicants respectfully traverse the rejection of claims 1-8 and 17-23 under 35 USC 102(b) as anticipated by, or in the alternative, under 35 USC 103 as obvious over WO '414.

4. Hodgson discloses film made from a base layer. The base layer has a heat sealable film layer on one or both surfaces of the base layer. The base layer comprises a blend of at least one very low density ethylene copolymer having a CBDI of 70% or higher and another polymer. The other polymer of the base layer is selected from the group consisting of polypropylene, low density polyethylene, linear low density polyethylene (LLDPE), polybutene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4 to C_{12} alpha olefin (see col. 4, lines 14-20 of Hodgson). However, Hodgson does not specify or describe the linear low density polyethylene as the "other polymer" of the base layer. Hodgson neither teaches nor suggests that the LLDPE which can be added to his film compositions is a heterogeneously branched polyethylene, as Applicants have taught and claimed.

Furthermore, as Inventor Chum's attached declaration shows, not all heterogeneously branched linear low density polyethylene has no more than about 10 % of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than about 1.3. Inventor Chum points out that about 30 % of Dowlex™ 2045 (a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company having a whole polymer density of about 0.92 g/cm^3) has

SHC > 1.3. Please note that the specification on p. 13, lines 26-31 describes Dowlex™ 2045 and that Figure 2 of the instant application shows its branching distribution. Thus not all heterogeneously branched ethylene polymers will have the properties necessary for improving the film performance.

Furthermore, the other component of the compositions used in Hodgson (as well as the other layer of the film) is "VLDPE." VLDPE is well known in the art to refer to a linear ethylene polymer having a very low density. Very low density polyethylene and ultra low density polyethylene (ULDPE) are used interchangeably in the art and refer to linear polyethylenes having densities less than 0.915 g/cm^3. *See* L.D. Cady, *Ultralow-density Polyethylene*, Modern Plastics Encyclopedia/89, mid October 1988 Issue, Volume 65, Number 11, p. 66 (copy enclosed). The substantially linear ethylene polymers used in Applicants' invention are patentably distinct from such VLDPE polymers, as discussed supra.

Applicants' invention is directed to film made from at least one substantially linear ethylene polymer and at least one heterogeneously branched ethylene polymer having not more than 10% of a polymer fraction having SHC ≥ 1.3. Since Hodgson is directed to linear ethylene polymers blended with some unknown and unspecified type of LLDPE, Applicants believe that Hodgson does not obviate the presently claimed invention. Accordingly, Applicants respectfully traverse the rejection of claims 1-8 and 17-23, as amended, under 35 USC 103 as being unpatentable over USP 5,206,075 (Hodgson).

CONCLUSION

Applicants respectfully submit that all of the rejections have been traversed. The claims, as amended, are believed to be in condition for allowance. Applicants respectfully request reconsideration and notice of allowance.

Respectfully submitted,

Noreen D Warrick

Noreen D. Warrick
Registration No. 34,573
Telephone: (409) 238-4510

May 12, 1994

The Dow Chemical Company
Patent Department
Building B-1211
Freeport, Texas 77541

MODERN PLASTICS ENCYCLOPEDIA

A PLASTICS PRIMER 4

KEY WORD INDEX 12

TEXTBOOK 17

Resins and compounds 17

Acetal 19
Acrylic 20
Allyl 128
Bismaleimides 128
Cellulosics 22
Epoxy 129
Fluoroplastics 24
Ketone-based resins 28
- Polyetheretherketone 28
- Polyetherketone 28

Melamine 140
Nitrile resin 28
Nylon 30
Phenolic 133
Polyamide-imide 32
Polyarylate 34
Polybutylene 36
Polycarbonate 38
Polyester, alkyd 134
Polyester, thermoplastic 41
- Liquid crystal polymers 41
- Polybutylene terephthalate: PBT 44
- Polyethylene terephthalate: PET 46
- Reinforced PET 48

Polyester, unsaturated 134
Polyetherimide 50
Polyethylene 63
- Branched polyethylene 70
- Ethylene acid copolymer 72
- Ethylene-ethyl acrylate 73
- Ethylene-methyl acrylate 74
- Ethylene-vinyl acetate 74
- Ethylene-vinyl alcohol copolymers 76
- High-density polyethylene 66
- HMW high-density polyethylene 67
- Ionomer 77
- Linear polyethylene 63
- Linear low-density polyethylene 64
- Low-density polyethylene 72
- Ultralow-density polyethylene 66
- UHMW polyethylene 69

Polyimide, thermoplastic 78
Polyimide, thermoset 135
Polymethylpentene 83
Polyphenylene ether, modified 83
Polyphenylene sulfide 84
Polypropylene 86
- Polypropylene homopolymer 88
- Polypropylene impact copolymers 88
- Polypropylene random copolymers 90

Polyurethane 136
Silicones 138
Styrenic resins 92
- ABS 92
- ACS 95
- Acrylic-styrene-acrylonitrile 96
- Crystal polystyrene 98
- Expandable polystyrene 104
- Impact polystyrene 103
- Olefin-modified SAN 105
- Polystyrene 97
- Styrene-acrylonitrile (SAN) 105
- Styrene-butadiene 106
- Styrene-maleic anhydride 106

Sulfone-based resins 108
- Polyarylsulfone 108
- Polyethersulfone 108
- Polysulfone 109

Thermoplastic elastomers 110
- Elastomeric alloy TPEs 112
- Engineering TPEs 112
- Olefinic TPEs 114
- Polyurethane TPEs 114
- Styrenic TPEs 116

Urea 140
Vinyl-based resins 118
- Chlorinated PVC 118
- Dispersion PVC 125
- PVC 118
- Suspension PVC 126
- Vinylidene chloride 127

Chemicals and additives 141

Antimicrobials 143
Antioxidants 143
Antistatic agents 144
Colorants 148
- Color concentrates 152
- Special colorants 150

Coupling agents 155
- Silanes 155
- Titanates 157

Emulsifiers 158
Flame retardants 161
- Smoke suppressants 162

Fluorinated intermediates 164
Foaming agents 166
Fragrances 170
Impact modifiers 172
Lubricants 173
Mold release agents 176
Organic peroxides 177
Plasticizers 180
Polyurethane foam catalysts 184
Stabilizers, heat 186
Stabilizers, ultraviolet 190
Viscosity depressants 192

Reinforced plastics and composites (including fillers) 193

Fibrous reinforcements 195
- Aramids 195
- Aramid hybrids 196
- Carbon/glass hybrids 199
- Ceramic fibers 199
- Glass fibers 202
- Metallic fibers 203
- Thermoplastic fibers 204

Fillers 206
- Glass fillers 207
- Mineral fillers 207

Thermoset molding compounds 208
- Bulk molding compounds (BMC) 210
- Prepregs 209
- Sheet molding compounds (SMC) 210
- Thick molding compounds (TMC) 212

Reinforced thermoplastics 214

Primary processing 215

Blow molding 217
- Blow molds 222
- Extrusion-blow molding 217
- Injection-blow molding 218
- Multilayer blow molding 220

Calendering 224
Casting 226
- Casting of acrylic 226
- Casting of film 232
- Casting of nylon 230

Compression molding 234
- Compression molds 238

Extrusion 242
- Extruder screen changers 250
- Extrusion dies 244
- Extrusion gear pumps 248

Foam processing 254
- Expandable PS foam molding 254
- Foam extrusion 256
- Polyurethane foam processing 262
- Thermoplastic structural foam molding 258

Injection molding 264
- Co-injection molding 268
- Injection molding thermoplastics 270
- Injection molding thermosets 272
- Injection molds 276
- Reaction injection molding 278

Radiation processing 276
Reinforced plastics/composites processing 282
- Automated tape placement 284
- Closed mold processing 286
- Continuous RP laminating 290
- Filament winding 291
- Open-mold processing 292
- Pultrusion and pulforming 294

Rotational molding 296
Thermoforming 301
- Solid phase pressure forming 304
- Thermoforming molds 308

Transfer molding 308

Auxiliary equipment 309

CAD/CAM/CAE 311
Chillers and associated equipment 314
- Chillers and cooling towers 314
- Liquid circulating temperature controls 314

Coating equipment 316
- Electrostatic coating 316
- Extrusion coating and laminating 316
- Roll coating 321

MID OCTOBER 1988 ISSUE VOLUME 65, NUMBER 11

Controls and tests 322
Controls and instrumentation 322
Testing by ASTM methods 327
Dryers 330
Film handling equipment 332
Biaxial orienting 332
Laminating 334
Granulators 336
Heaters 340
Materials handling 342
Mixing and compounding 344
Color measurement and control 350
Dry solids mixers 344
Fluxed melt mixers 345
Liquid and paste mixers 348
Motionless mixers 349
Pelletizing and dicing 352
Robots 353

Fabricating and finishing 355
Assembly of fabricated parts 357
Adhesive bonding 357
Electromagnetic bonding 359
Induction bonding 362
Insert bonding 362
Radio frequency sealing 364
Spin welding 366
Thermal welding 368
Ultrasonic sealing 370
Vibration welding 372
Decorating and printing 372
Electroplating and sputtering 372
Embossing 376
Hot stamping 377
In-mold decorating with coatings 378
In-mold decorating with foils 380
Printing 381
Vacuum metallizing 384
EMI shielding and electrostatic discharge 385
By internal compounding 385
By mechanical means 386
By surface treatments 387
Post-production handling 388
Cutters 388
Pipe, tubing, and profile takeoff 389
Sheet takeoff equipment 390
Slitting and winding 392
Stamping reinforced sheet 396

Design 397
Redesigning with plastics: an introduction 399
Designing with plastics 404
Designing for rigidity and strength under static load 406
Selecting plastics for elevated temperature performance 409
Dynamic mechanical properties of plastics by torsion pendulum 413
Selecting plastics for chemical resistance 414
Selecting plastics for fatigue resistance 417
Selecting plastics for stress relaxation 419
Selecting plastics for impact resistance 423
Selecting plastics for flame retardance and smoke suppression 426
Selecting plastics for dielectric loss properties 428

ENGINEERING DATA BANK

Materials
Colorants 560
Dimensional stability 626
Fatigue 620
Flame retardants 553
Foams 656
Optical brighteners 573
Outdoor exposure resistance 639
Poisson's ratio 653
Resins and compounds 576
Specifications/materials 509
Temperature index 659
UV stabilizers 574

Machinery
Blow molding machines 701
Compression molding machines 711
Extruders 722
Granulators 729
Injection molding machines 735
Reaction injection molding machines 743
Thermoforming machines 751

BUYERS' GUIDE

Alphabetical index of companies and addresses 767
Classified index of products and services 882
Products and services 793
Custom processors and converters 870
Film, sheet, shapes, laminates 815
Foamed plastics 806
Instruments and controls 850
Machinery and equipment 823
Modifiers, additives, and fillers 807
Reinforcements and composites 821
Resins and compounds 793
Specialized services 860
Supplies 854

Advertisers' index 892

Advertisers' literature 887

Reader service cards 895-902

PERMISSIONS: Where necessary, permission is granted by the copyright owner for libraries and others registered with the Copyright Clearance Center (CCC) to photocopy any page herein for the flat fee of $5.00 per copy of the page. Payment should be sent directly to the CCC, 21 Congress St., Salem, MA 01970. CCC copying done for other than personal or internal reference use without the express permission of McGraw-Hill is prohibited. Requests for special permission or bulk orders should be addressed to Modern Plastics Reprint Dept., 1221 Ave. of the Americas, New York, NY 10020. ISSN 0026-8275.

Editor
Rosalind Juran

Editorial director
Robert J. Martino

Assistant editor
Jean Corvington

Associate Publisher
Robert B. Crosland, III

Technical editor
James F. Carley

Group Publisher
Alan R. Morris

Engineering editor
George Smoluk

Art director
Bob Barravecchia

Graphic Design
Rocco Lotito

Officers of McGraw-Hill, Inc.
Joseph L. Dionne, Chairman, President and Chief Executive Officer; Robert N. Landes, Executive Vice President, General Counsel and Secretary; Frank D. Penglase, Senior Vice President, Treasury Operations.

Officers of McGraw-Hill Information Services Company
Walter D. Serwatka, President; Robert D. Daleo, Senior Vice President, Finance; Norbert Schumacher, Group Vice President; Alan R. Morris, Group Publisher.

Please mail all circulation correspondence, subscription orders, and change of address notices to Modern Plastics, Fulfillment Mgr., P.O. Box 430, Hightstown, NJ 08520. Postmaster: Send Form 3579 to Fulfillment Manager, Modern Plastics, P.O. Box 430, Hightstown, NJ. Modern Plastics has no connection with any company of similar name. Modern Plastics printed in U.S.A. Publication office: 1221 Ave. of the Americas, New York, NY 10020. Modern Plastics published 13 times a year, monthly, plus special Modern Plastics Encyclopedia issue. Postage paid at Montreal, P.Q. Registration Number 9406. Available only by paid subscription. Please allow 4 to 8 weeks for shipment. Modern Plastics solicits subscriptions from management, engineering, manufacturing, R&D, scientific and technical, purchasing and marketing men and women involved in the plastics field. Publisher reserves the right to refuse any subscription. Subscription rates for manufacturing, engineering, and R&D companies; also, government and schools (incl. Modern Plastics Encyclopedia issue): in the U.S. and its possessions, 1 yr. $36, 2 yrs. $54, 3 yrs. $72; in Canada, 1 yr. $CDN 52, 2 yrs. $CDN 78, 3 yrs. $CDN 104. Rate for other companies in the U.S. and its possessions $42 per yr.; Canada $CDN 60 per yr. Single copies (except for Encyclopedia issue) $6 each, $CDN 8.00. For subscriber service, call collect 215-630-9724 in the U.S. except Alaska and Hawaii. The name 'Modern Plastics' is Registered ® U.S. Pat Off., including Reg., mark Plastiscope ®. Copyright © 1988 McGraw-Hill, Inc. All rights reserved. PERMISSIONS: Where necessary, permission is granted by the copyright owner for libraries and others registered with the Copyright Clearance Center (CCC) to photocopy any article herein for the flat fee of $5.00 per copy of the article. Payment should be sent directly to the CCC, 21 Congress St., Salem, MA 01970. Copying done for other than personal or internal reference use without the express permission of McGraw-Hill is prohibited. Requests for special permission or bulk orders should be addressed to the publisher. ISSN 0026-8275/85 $5.00.

Ultralow-density polyethylene

By L.D. Cady

Ultralow-density polyethylene and very low-density polyethylene are essentially synonymous terms referring to the category of linear polyethylenes with densities below 0.915 g./cc. Current technology provides a lower density limit between 0.880 and 0.890 g./cc.

The importance of these polymers stems from their unique combination of strength, sealability, flexibility, and optical properties. ULDPEs offer puncture, impact, tear, and optical properties superior to conventional linear low density polyethylenes (LLDPE), with sealing and flexibility properties comparable to 7 to 18% vinyl acetate copolymers (EVA).

Chemistry and properties

ULDPEs are manufactured by copolymerizing ethylene and selected alpha-olefins using a transition metal catalyst system. The polymers may employ a single alpha-olefin comonomer or a combination of comonomers.

The most common and commercially important comonomers are octene-1, hexene-1, butene-1, and 4-methylpentene-1. Comonomer content determines the density of the polymer, with increasing content resulting in lower density.

Additionally, it is well understood that employment of longer comonomers, i.e., octene-1 vs. butene-1, results in improvements in tear strength, puncture resistance, impact strength, and toughness of the polymer. This relationship is evident for conventional density LLDPEs, and enhanced for ULDPEs.

The lower density of ULDPE compared to other linear polyethylenes results in a softer, lower-modulus polymer. In turn, the lower modulus provides for better energy-absorbing characteristics of the polymer, which can yield superior impact and puncture resistance compared to LLDPEs. Additionally, ULDPEs are comparable in modulus to 7 to 18% vinyl acetate copolymers, but their linear nature results in significant advantages in impact, puncture, and tear resistance.

The softening point of linear polyethylene decreases as density decreases; therefore, the sealing range and minimum sealing temperature of ULDPE is significantly improved over LLDPE. ULDPE also offers excellent hot tack strength and sealability through contamination, both important attributes in film packaging applications.

The nonpolar nature of ULDPE offers better chemical resistance and thermal stability than polar copolymers; however, adhesion to polar substrates is generally inferior to that attainable by EVA. The adhesion of ULDPE to other polyethylenes, acid copolymers, and polypropylene is generally excellent.

The permeability of linear polyethylene is a function of the crystallinity of the polymer. Consequently, the lower crystallinity of ULDPE results in increased permeability to gases compared to higher density linear polymers, but similar to LDPE and EVA copolymers.

Processing

The rheological properties of ULDPE are similar to other linear polyethylenes, and dictated by the molecular weight and molecular weight distribution (MWD). A variety of grades ranging from fractional melt index to greater than 25 melt index, with narrow or broad MWDs, are available within this class of polymers.

ULDPEs can typically be extruded on existing polyethylene equipment, particularly equipment designed to process LLDPE. Modifications to high-shear, high-pressure equipment may be necessary to provide optimum processing of these polymers.

ULDPEs have very high thermal stability compared to polar copolymers. This results in the ability to run melt temperatures above 500°F., with the preferred range being 430 to 480°F.

In film manufacture, take-up and conversion of ULDPE is similar to EVA based on the modulus similarities. The toughness of ULDPE may also require improved slitting technology.

Applications

Most applications requiring superior toughness, puncture, tear, flexibility, and sealability are likely candidates for ULDPE. The unique combination of properties these polymers provide makes them suitable for film extrusion (especially coextrusion and lamination), blow molding, injection molding, sheet extrusion, filled systems, and profile and tubing applications. Additionally, several grades of these polymers conform to FDA regulations for direct food contact.

Specific film end-use applications include: meat, cheese, and poultry packaging, stretch film, bag-in-box, shrink film, heavy duty film, frozen food packaging, disposable gloves, medical packaging and film, and heat seal layers. Coextrusion and blending with HDPE and PP to improve tear and impact strength of those structures is also a significant application for these polymers.

Commercial information

ULDPE prices generally increase with decreasing density, reflecting increased comonomer costs. As of Jan. 1, 1988, film extrusion grades from 0.912 to 0.905 densities ranged in price from 60 to 65¢/lb., bulk railcar, respectively. □

L.D. Cady is Project Leader, Dow Chemical Co., Hwy. 288, Building B-1607, Freeport, TX 77541.

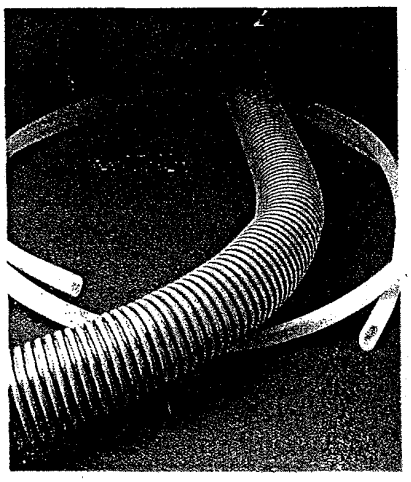


Fig. 1: ULDPE provides extruded tubing with flexibility over a range of temperatures, puncture resistance, and effective pigmentation. [Photo, Dow Chemical Co.]

High-density polyethylene

By Daniel D. Bussone

High-density polyethylene is a highly crystalline, lightweight thermoplastic. Outstanding characteristics are chemical resistance, toughness (even at low temperatures), dielectric properties, water vapor impermeability and relatively high softening temperature.

Manufacturing methods

There are three basic manufacturing techniques for the production of HDPE: particle form slurry reactors, tandem reactors, and gas phase reactors.

Particle form slurry methods, which are the most widely used processes, produce HDPE resins for all processing methods.

In particle form slurry processes, a supported transition metal catalyst slurried in a diluent is circulated in a closed-loop reactor at a low pressure and low temperature. Ethylene, which is dissolved in the diluent, reacts with the catalyst to form solid HDPE particles. The particles are dried, combined with additives, and extruded as pellets.

Tandem reactor methods have two particle form slurry reactors that are run in series or parallel, which permits short chain side branches to be regularly introduced into the linear molecular chains. This method yields lower-crystallinity resins having improved environmental stress cracking resistance, good water vapor permeability, impact strength, and enhanced processability.

Tandem reactors are used mainly to

Daniel D. Bussone is High Density Polyethylene Business Manager for Quantum Chemical Corp., USI Div., P.O. Box 429550, Cincinnati, OH 45249.

MAIL ROOM MAY 18 1994 TRADEMARK OFF.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.

Serial No.: 08/054,379 Group Art Unit: 1505

Filed: April 28, 1993 Examiner: D. WU

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON D.C. 20231, On May 13, 1994

DATE OF DEPOSIT

Jan Alverson

PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Jan Alverson

SIGNATURE OF PERSON SIGNING CERTIFICATE

5-13-94

DATE OF SIGNATURE

RECEIVED JUN 0 1 1994 GROUP 150

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

DECLARATION UNDER CFR 1.132

Pak-Wing Steve Chum declares and states:

THAT, he obtained a Bachelor of Science degree in Chemistry from Hong Kong Baptist College in 1970, a Master of Science degree in Chemistry from Northern Michigan University in 1974, and a PhD in Physical Organic Chemistry from Oregon State University in 1978;

THAT, he joined The Dow Chemical Company (Midland, MI) in 1980 as a Senior Research Chemist, was promoted to Project Leader in 1983, to Research Leader in 1985, to Research Associate in 1988, to Associate Scientist in 1991, and to his present position as Senior Associate Scientist in 1994;

THAT, during the last fourteen years, he has focused his research effort in the area of thermolplastics and plastic foams;

THAT, he currently leads the effort in Polymer Materials Science research for The Dow Chemical Company (Texas Operations);

That, he is a member of the American Chemical Society, a member of the Board of Directors of the Society of Plastic Engineers, a member of the Board of Industry Advisors for Case Western Reserve University, and was a Visiting Professor for the Michigan Macromolecular Institute (1987-1988);

THAT, he received the American Chemical Society Outstanding Scientific Achievement Award in 1993;

THAT, he served as author or co-author of the publications 1992-1994 listed in Attachment One;

That, he is an inventor in the above-identified Application and is therefore familiar with the Application and the Office Action thereon;

THAT, polyethylenes, including linear low density polyethylene, can be characterized by various slope of strain hardening coefficient profiles;

THAT, not all linear low density polyethylene is characterized as having no more than about 10 percent of a polymer fraction having a slope of strain hardening coefficient greater than about 1.3;

THAT, for example, about 30 percent of DOWLEX™ 2045 (a heterogeneously branched linear low density ethylene/1-octene copolymer made by The Dow Chemical Company having a whole polymer density of about 0.92 g/cm³) is characterized by a slope of strain hardening coefficient greater than about 1.3;

THAT, films fabricated from polymer blends with compositions comprising: (a) a heterogeneously branched ethylene polymer having a density from about 0.93 to 0.965 g/cm³ and are characterized as having no more than about 10 percent of a polymer fraction having a slope of strain hardening coefficient greater than about 1.3, and (b) a homogeneously branched substantially linear ethylene/α-olefin interpolymer, are improved over films fabricated from conventional linear low density polyethylene, such as are prepared using Ziegler-Natta catalysts comprising a heterogeneously branched ethylene polymer characterized as having more than about 10 percent of a polymer fraction having a slope of strain hardening coefficient greater than about 1.3, in that the former are characterized by greatly improved dart impact A values (see Table 3 at page 25 of the specification).

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date May 12, 1994

Pak-Wing Steve Chum

PUBLICATIONS BY PAK-WING STEVE CHUM
(1992 to 1994)

1. "Computer Modeling of (110) Adjacent Re-entry of Polyethylene Molecules"; P. S. Chum (Dow Chemical Co.) and Prof. P. J. Phillips (University of Tennessee), et al., *Macromolecules, Vol. 27, No. 3, pp. 656, (1994)*

2. "Effect of Chain Microstructure on Modulus of Ethylene-alpha-Olefin Copolymers"; P. S. Chum, K. Sehanobish, C. I. Kao, et al., (all of Dow Chemical Company), *Journal of Applied Polymer Science, Vol. 51, pp. 887 (1994)*

3. "New Polyolefin Based Elatomers for TPO Impact Modification", P. S. Chum, H. C. Silvis C. I. Kao, (all of Dow Chemical Company), *Proceedings of the SAE International Congress & Exposition, Paper # 940435, February, 1994*

4. "Morphology and Deformation Behavior of Homogeneous Polyolefin Copolymers made with Insite* Technology", P. S. Chum, R. Guerra, et al., (All of Dow Chemical Co.), *Proceedings of SPE Antec' 94, May, 1994*

5. "Bridging the Polyethylene Lifetime under Fatigue and Creep Conditions with its Crystallization Behavior", P. S. Chum (Dow Chemical Company) and Prof. A. Chudnovsky (University of Illinois at Chicago), et al., *Journal of Applied Polymer Science, Vol 49, pp. 863-875 (1993)*

6. "Synthesis of a Stable Foamable, Gold-Containing Organic Carboxylate Polyethylene Polymer"; P. S. Chum (Dow Chemical Co.), Prof. J. P. Fackler (Texas A&M University), et al., *Journal of Polymer Science: Part A: Polymer Chemistry, Vol 31, PP. 2353 (1993)*

7. "Insite* Technology Based Polyolefin Elatomers for Impact Modification", P. S. Chum, H. C. Silvis and C. I. Kao (All of Dow Chemical Company), *Proceedings of the 1993 SPO International Polymer Conference, PP. 247 (1993)*

8. "Effect of Vinyl Chain-Ends on the Melt Viscoelatics Properties of Radiation Crosslinked Polyethylenes", P. S. Chum (Dow Chemical Company), *Journal of Plastics Film and Sheeting, Vol. 8, No. 1, PP. 37, (1992)*

9. "Influence of Extruder Conditions on Orientation Distribution in LLDPE Blown Films", P. S. Chum and S. V. Karande (All of Dow Chemical Co.), *Journal of Plastics Film and Sheeting, Vol. 8, No. 1, PP. 74, (1992)*

ATTACHMENT ONE