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(54) **Title:** POLYMER BLENDS

(57) **Abstract:** Novel polymer blends comprise (a) 90 - 97% by weight of a copolymer of ethylene and an alpha olefin having from 3 to 10 carbon atoms, said copolymer having (i) a density in the range 0.910 to 0.940 g cm<sup>-3</sup>, (ii) a melt index (190°C/2.16 kg), MI<sub>1</sub> < 5, and (iii) molecular weight distribution (M<sub>w,cc</sub>/M<sub>n,cc</sub>, by classical GPC) in the range 2.0 - 5.0, and (b) from 3 - 10% by weight of a low density polyethylene polymer having (i) a density from 0.910 to 0.920 g cm<sup>-3</sup>, (ii) a melt index (190°C/2.16 kg), MI<sub>2</sub> > 2, and (iii) a melt elastic modulus G'(G"= 500 Pa) > 140 Pa at 190°C. wherein the sum of (a) and (b) is 100%. The copolymer component (a) may be prepared by use of metallocene catalyst systems and the novel blends exhibit an improved balance of processability and mechanical properties and are particularly useful for film applications.



WO 2013/079654 A1

## POLYMER BLENDS

The present invention relates to polymer blends and in particular to polymer blends comprising ethylene - alpha-olefin copolymers and low density polyethylenes. The copolymers may typically be produced using metallocene catalysts and the polymer blends exhibit high melt strength and are particularly suitable for film applications.

There are a number of different types of known polymers which may suitably be divided by means of their density. For example traditional Ziegler-Natta catalysts have been used to prepare linear low density polyethylenes (LLDPE's) having densities in a typical range of 0.915 to 0.928 g cm<sup>-3</sup>. Medium density polyethylenes with typical densities in the range 0.929 to 0.940 g cm<sup>-3</sup> and high density polyethylenes with densities greater than 0.940 g cm<sup>-3</sup> are also well known. Since the mid-90's, linear low density polyethylenes (LLDPE's) have also been produced with densities below 0.915 g cm<sup>-3</sup>.

The linear low density polyethylenes (LLDPE's) have more recently been prepared by use of single site catalyst systems and in particular by use of metallocene catalyst systems. Our earlier publications WO 97/44371, WO 00/68285, WO 06/085051 and WO 08/074689 describe the preparation of high performance linear low density copolymers prepared by use of monocyclopentadienyl metallocene complexes. The polymers have been found to exhibit good processing characteristics and to be particularly suitable for use in the preparation of films such as blown films having improved mechanical and optical properties.

The processing behaviour of a polyethylene product is typically characterised by (i) the extrudability behaviour of the polymer melt within the extruder, in particular through the extrusion die, and (ii) the behaviour of the extrudates under the post-extruder processes associated with the various polymer processing applications (e.g., in open surface processes like film blowing, extrusion coating, fibre spinning, etc.).

The extrudability characteristics can be evaluated by, for example, the ease of extrusion of the polyethylene composition that makes possible to reduce energy consumption at given output rate (Q) or to increase machine output at a given energy consumption. For example, this extrusion energy consumption can be characterised broadly by an Energy Index (EI) defined by some of the key extrusion parameters:

$$\text{Energy Index (EI)} = [\text{Screw Speed (S)} \times \text{Motor Load (A)}] / [\text{Output Rate (Q)}],$$

where Screw Speed in unit of revolutions per minute (rpm), Motor Load in current Ampere (A) and Output rate in kilograms per hour (kg/h).

Hence, it is expected that materials with lower viscosity at polymer extrusion rates (typically at shear rates of the order  $500 \text{ s}^{-1}$  for film blowing process) will have lower Energy Index, i.e., a better extrudability, lower motor load and lower melt-pressure. The required processing rheology can often be achieved by reducing the average molecular weight (i.e. increasing melt-index) of the polymer, or increasing the breadth of its molecular weight distribution, or the presence of long chain branching, or the combination of the above polymer molecular structure and properties.

On the other side, the post-extruder processability is often characterised as the ability and stability of the extrudate in forming the desired product geometry, thickness and size, etc., under a given processing equipment and conditions. For example, in the case of blown film extrusion processes, the bubble stability is a key attribute that makes possible to achieve large diameter bubbles, and/or thinner film thickness, without surface imperfections (e.g., no sharkskin and/or melt fracture), at highest possible output rates. It is commonly observed that a better bubble stability is obtained with compositions having specific rheological features, particularly higher melt strength and extensional rheological properties (e.g., strain hardening). An increase in high molecular weight fraction (by reducing the melt-index or increasing the breadth of the molecular weight distribution, for instance) and/or the presence of long chain branching in the polyethylene compositions results in higher melt strength, hence better bubble stability.

Methods have been developed in order to improve the processing of such LLDPEs for film applications. However such improvements in extrudability or processability are often accompanied by a reduction in mechanical properties in particular with respect to film applications. In addition, variations in the molecular structure of the polyethylene to improve the extrudability may have a detrimental effect on the bubble stability; for instance, an increase in melt-index will have a positive impact on the extrudability as the polymer will be more fluid, but the bubble stability during a blown film extrusion will also be badly affected (i.e., lower melt-strength at higher melt-index).

LLDPEs containing long chain branching have been developed to improve the balance of processability and mechanical properties. For example WO

2009/109367 describes polymers prepared by use of bridged bis-indenyl zirconocene complexes in the gas phase and are defined in terms of melt index ratio,  $I_{21}/I_2 > 35$  indicative of the presence of long chain branching.

For some applications LLDPEs have been blended with other polymers such as low density polyethylenes (LDPEs). One such application is extrusion coating and our earlier publication WO 05/001933 describes blends based on high performance linear low density copolymers with LDPEs. Polymer blends having at least 25% of the LDPE component are reported.

EP 1081 166 describes blends of 60 - 95 wt% ethylene -alpha-olefin copolymer and 5 - 40 wt% of a LDPE. The copolymers typically have a density in the range 0.910 - 0.930 g cm<sup>-3</sup> and a melt index in the range 0.3 - 5 g/10 mins. The LDPE component of the blends typically has densities in the range 0.922 - 0.924 g cm<sup>-3</sup>.

WO 00/68285 describes LLDPE copolymers having a unique combination of properties in particular a narrow molecular weight distribution ( $M_w/M_n$ ) in the range 2 to 3.4 and an activation energy in the range 28 to 45 kJ/mol. These copolymers may be produced in the gas phase using metallocene catalysts and the reference discloses generally that the copolymers may be blended with other polymer components such as low density polyethylenes (LDPE).

WO 00/09594 describes blends of LLDPEs and LDPEs for high clarity polyethylene compositions in which the LDPE component is present in very low amounts ( $\leq 3$  wt%). The improvements are directed to optical properties at these very low amounts of LDPE however there are no indications with respect to processability and extrudability.

US 2002/0143123A1 describes "substantially non-blended" or "substantially unblended" LLDPEs, having a melt index ratio  $I_{21}/I_2$  ( $MIR \equiv HLMI/MI_2$ ) in the range of from 40 - 90 at an MI of 0.7 g/10 min, as embodiments of having less than 10 wt%, or less than 5 wt%, or less than 3 wt%, or 0 wt% of a separate, branched polymer, for example, LDPE, wherein the said copolymer has a melt strength (MS) in the range of from 5 - 20 cN.

EP0095253A1 describes blends of LLDPEs and LDPEs for improved and good mechanical properties in which the high pressure polymer having a melt index greater than 6 and not greater than 20, and a melt index ratio  $I_2i/I_2$  ( $MIR \equiv HLMI/MI_2$ ) below 50.0.

However, there are no indications with respect to the melt elasticity and melt strength characteristics of the high pressure polymer that are novel in the invention.

For extrusion coating applications, EP1777238B describes blends of an olefin polymer prepared in the presence of a transition metal catalyst with 5 - 40 wt% LDPEs having a melt index ( $MI_2$ ) in the range 2.5 - 10, where the rheological properties of the latter are characterised by very high molecular weight averages ( $M_w = 400 - 600$  kg/mol, and  $M_z = 2000 - 4000$  kg/mol) and very broad molecular weight distribution (polydispersity index  $M_w/M_n$  in the range 20 - 50) measured by classical Size Exclusion Chromatography (SEC), or classical Gel Permeation Chromatography (GPC), with conventional calibration method using narrow molecular weight linear polystyrene standards.

There is still however a demand for polymers having an improved balance of properties - processability/mechanical/extrudability - in particular for film applications.

We have now surprisingly found that polymer blends may be prepared based on LLDPE's and LDPE's wherein the LDPE's are present in low amounts compared with previous known blends. The LLDPE's have a narrow molecular weight distribution but which have unique melt index and melt rheological properties thus leading to improved blends in particular for high performance film applications.

Thus according to a first aspect of the present invention there is provided a polymer blend comprising

(a) 90 - 97% by weight of a copolymer of ethylene and an alpha olefin having from 3 to 10 carbon atoms, said copolymer having

- (i) a density in the range 0.910 to 0.940 g cm<sup>-3</sup>,
- (ii) a melt index (190°C/2.16 kg),  $MI_2 < 5$ , and
- (iii) molecular weight distribution ( $M_{w,c}/M_{n,c}$ , by classical GPC) in the range 2.0 - 5.0, and

(b) from 3 - 10% by weight of a low density polyethylene polymer having

- (i) a density from 0.910 to 0.920 g cm<sup>-3</sup> and
- (ii) a melt index (190°C/2.16 kg),  $MI_2 > 2$ , and
- (iii) a melt elastic modulus  $G'(G'' = 500 \text{ Pa}) \geq 140 \text{ Pa}$  at 190°C.

wherein the sum of (a) and (b) is 100%.

The copolymers of component (a) of the polymer blends of the present invention preferably have density in the range  $0.912 - 0.935 \text{ g cm}^{-3}$ , more preferably in the range  $0.915 - 0.935 \text{ g cm}^{-3}$  and most preferably in the range  $0.916 - 0.926 \text{ g cm}^{-3}$ .

The copolymers of component (a) preferably have a melt elastic modulus  $G'$  ( $G'' = 500 \text{ Pa}$ ) at  $190^\circ\text{C}$  in the range  $25 - 70 \text{ Pa}$ , and most preferably in the range  $30 - 70 \text{ Pa}$ .

The copolymers of component (a) preferably have a melt index ( $190^\circ\text{C}/2.16 \text{ kg}$ ),  $\text{MI}_2$  in the range  $0.1 - 4.0$ , and most preferably in the range  $0.5 - 3.0$ .

The copolymers of component (a) have a melt index ratio  $I_2 i/I_2$  ( $\text{MIR} = \text{HLMI}/\text{ML}$ ) less than 35, and preferably more than 15, and more preferably in the range of  $18 - 25$ , and most preferably in the range  $19 - 23$ .

The copolymers of component (a) preferably have a molecular weight distribution ( $M_{w-c}/M_{n-c}$ , by classical GPC) in the range  $2.0 - 4.2$ , more preferably in the range  $3.0 - 4.2$  and most preferably in the range  $3.0 - 4.0$ .

The copolymers of component (a) typically exhibit a flow activation energy ( $E_a$ ) at  $190^\circ\text{C}$  in the range  $28 - 45 \text{ kJ/mol}$ , more preferably in the range  $30 - 40 \text{ kJ/mol}$  and most preferably in the range  $30 - 35 \text{ kJ/mol}$ .

The copolymers of component (a) typically exhibit a Branching Index (by SEC/MALLS), or Branching Contraction Factor,  $g < 1$ , preferably in the range  $0.80 - 0.92$ .

The copolymers of component (a) typically exhibit a Branching Index which has been empirically corrected for short chain branching effect,  $g_{\text{corrected}} < 1$ , or an equivalent Long Chain Branching Contraction Factor,  $g_{\text{LCB}} < 1$ , both preferably in the range  $0.80 - 0.99$  and most preferably in the range  $0.84 - 0.99$ .

The copolymers of component (a) of the blends exhibit melt strength pressure derivatives at  $190^\circ\text{C}$ ,  $\delta(\text{MS})/\delta P$ , in the range  $0.10$  to  $0.45$  and preferably in the range  $0.15$  to  $0.25 \text{ cN/MPa}$ , wherein  $\text{MS}$  is the melt strength of the copolymer in  $\text{cN}$  and  $P$  is the extrusion pressure of the copolymer in  $\text{MPa}$ .

The copolymers of component (a) of the blends also exhibit a melt strength shear rate derivative at  $190^\circ\text{C}$ ,  $\delta(\text{MS})/\delta(\log \dot{\gamma})$  in the range  $1.5 - 6.0 \text{ cN}$  and most preferably in the range  $2.5 - 5.0 \text{ cN}$ , wherein  $\text{MS}$  is the melt strength of the copolymer in  $\text{cN}$  and  $\dot{\gamma}$  is the capillary shear rate of the copolymer in  $\text{s}^{-1}$ .

The LDPE component (b) of the polymer blends preferably has a density in the range 0.912 - 0.918 g cm<sup>-3</sup>, and most preferably in the range 0.914 to 0.918 g cm<sup>-3</sup>.

The LDPE component (b) preferably has a melt index (190°C/2.16 kg), MI<sub>2</sub> in the range 3 - 8, and most preferably in the range 3 - 6.

5 The LDPE component (b) preferably has a high load melt index (190°C/2.16 kg), (HLMI) in the range 80 - 160, more probably in the range 100 - 160, and most preferably in the range 130 - 160.

The LDPE component (b) preferably has a melt index ratio, I<sub>2</sub>/I<sub>1</sub> (MIR ≡ HLMI/ML), at 190°C in the range 35 - 54, and most preferably in the range 35 - 45.

10 The LDPE component (b) preferably has a molecular weight distribution (M<sub>w,cc</sub>/M<sub>n,cc</sub>, by classical GPC) in the range 5 - 15, more preferably in the range 7 - 14.

The LDPE component (b) preferably has a melt elastic modulus G' (G'' = 500 Pa) at 190°C, more preferably greater 145 Pa, and most preferably in the range 150 - 185 Pa.

15 The LDPE component (b) typically exhibit a flow activation energy (E<sub>a</sub>) at 190°C in the range 40 - 60 kJ/mol, more preferably in the range 40 - 55 kJ/mol and most preferably in the 45 - 55 kJ/mol.

The LDPE component (b) preferably has a melt strength at shear rate of 100 s<sup>-1</sup>, MS(100 s<sup>-1</sup>) at 190°C of ≥ 10 cN, more preferably of ≥ 12 cN and most preferably in the range 12 - 20 cN.

20 The LDPE component of the blends of the present invention preferably has a weight-average molecular weight ratio, M<sub>w-LS</sub>/M<sub>w-calib</sub> > 2.5 and more preferably greater than 3.

M<sub>w-LS</sub>/M<sub>w-calib</sub> represents the weight-average molecular weight ratio determined by use of SEC/MALLS, full details of which are provided in the experimental section.

25 The novel polymer blends of the present invention preferably comprise 92 - 97 % by weight of component (a) and 3 - 8% by weight of component (b), more preferably comprise 93 - 96 % by weight of component (a) and 4 - 7% by weight of component (b).

The blends of the present invention comprise features of the individual components (a) and (b) to provide the technical advantages of excellent processing and extrusion  
30 behaviour without jeopardizing the mechanical properties of resultant films.

Thus according to the present invention there is provided polymer blends as described hereinbefore wherein component (a) has a melt strength pressure derivative at

190°C 5(MS)/5P in the range 0.10 to 0.45 and component (b) has a melt strength at shear rate of 100 s<sup>-1</sup>, MS(100 s<sup>-1</sup>) at 190°C of ≥ 10 cN.

The blends also comprise those wherein component (a) has a Long Chain Branching Contraction Factor,  $g_{LCB} < 1$  and component (b) has a weight-average molecular weight ratio,  $M_{w-L}/M_{w-a} > 2.5$ .

The blends also comprise those wherein component (a) has a melt index ratio  $I_2/I_1$  less than 35 and component (b) has a High Load Melt Index, HLMI (190°C/21.6 kg) in the range 80 - 160.

The blends also comprise those wherein component (a) has a molecular weight distribution ( $M_{w-c}/M_{n-c}$ , by classical GPC) in the range 2.0 to 4.2 and component (b) has a molecular weight distribution ( $M_{w-c}/M_{n-c}$ , by classical GPC) in the range 5 - 15.

The copolymers of component (a) of the present invention may typically be prepared by use of catalyst systems comprising transition metal compounds. The transition metal compounds may be used in the presence of a suitable cocatalyst and may be supported.

The copolymers of component (a) are most preferably prepared by use of metallocene catalyst systems.

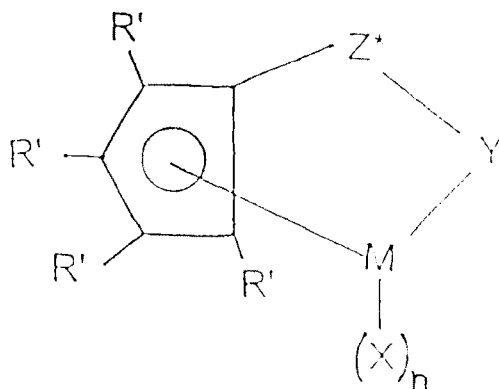
A preferred catalyst system for making the polyethylene copolymers utilised in the invention is a metallocene catalyst system comprising a monocyclopentadienyl metallocene complex having a 'constrained geometry' configuration together with a suitable activator. Examples of such monocyclopentadienyl or substituted monocyclopentadienyl complexes are described in EP 4 168 15 A, EP 4 180 44 A, EP 4 204 36 A and EP 5 512 77 A. This type of catalyst system is known to exhibit high activity and to give relatively low catalyst residues in the final resin.

Particularly suitable monocyclopentadienyl or substituted monocyclopentadienyl complexes may be represented by the general formula  $CpMX_n$  wherein Cp is a single cyclopentadienyl or substituted cyclopentadienyl group optionally covalently bonded to M through a substituent, M is a Group IVB metal bound in a  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group, X each occurrence is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral



Lewis base ligands having up to 20 non-hydrogen atoms or optionally one X together with Cp forms a metallocycle with M and n is dependent upon the valency of the metal.

Preferred monocyclopentadienyl complexes have the formula:



5

wherein:-

R' in each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms,

15 Y is -O-, -S-, -NR\*-, -PR\*-,

M is hafnium, titanium or zirconium,

Z\* is SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>SiR\*<sub>2</sub>, CR\*<sub>2</sub>CR\*<sub>2</sub>, CR\*=CR\*, CR\*<sub>2</sub>SiR\*<sub>2</sub>, or

GeR\*<sub>2</sub>, wherein:

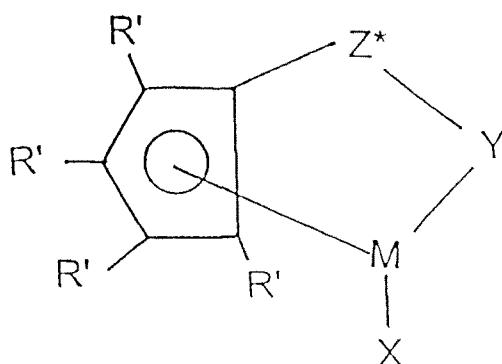
R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

20 R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system.,

and n is 1 or 2 depending on the valence of M.

Examples of suitable monocyclopentadienyl complexes are (tert-butylamido) dimethyl (tetramethyl- $\eta^5$ -cyclopentadienyl) silanetitanium dichloride and (2-methoxyphenylamido) dimethyl (tetramethyl- $\eta^5$ -cyclopentadienyl) silanetitanium dichloride.

- 5 Particularly preferred metallocene complexes for use in the preparation of the copolymers of the present invention may be represented by the general formula:



10

wherein:-

- R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germlyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together  
15 form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$ -complex with M;

Y is -O-, -S-, -NR\*-, -PR\*-,

20

M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ , wherein:

$R^*$  each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

$R^*$  having up to 10 non-hydrogen atoms, and optionally, two  $R^*$  groups from  $Z^*$  (when  $R^*$  is not hydrogen), or an  $R^*$  group from  $Z^*$  and an  $R^*$  group from Y form a ring system.

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably  $R'$  is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2  $R'$  groups (except hydrogen) are linked together, the entire

$C_5R'_4$  group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula  $-N(R'')$  or  $-P(R'')$  wherein  $R''$  is  $C_{1-10}$  hydrocarbyl.

Most preferred complexes are amidosilane - or amidoalkanediy l complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes which may be used are those disclosed in WO 95/00526 and these are incorporated herein by reference. A particularly preferred complex is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3-pentadiene.

Suitable cocatalysts for use in the preparation of the novel copolymers of the present invention are those typically used with the aforementioned metallocene complexes. These include aluminoxanes such as methyl aluminoxane (MAO), boranes such as tris(pentafluorophenyl) borane and borates.

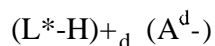
Aluminoxanes are well known in the art and preferably comprise oligomeric linear and/or cyclic alkyl aluminoxanes. Aluminoxanes may be prepared in a number of ways and preferably are prepared by contacting water and a trialkylaluminium compound, for

example trimethylaluminium, in a suitable organic medium such as benzene or an aliphatic hydrocarbon. A preferred aluminoxane is methyl aluminoxane (MAO).

Other suitable cocatalysts are organoboron compounds in particular triarylboron compounds. A particularly preferred triarylboron compound is tris(pentafluorophenyl)  
5 borane.

Other compounds suitable as cocatalysts are compounds which comprise a cation and an anion. The cation is typically a Bronsted acid capable of donating a proton and the anion is typically a compatible non-coordinating bulky species capable of stabilizing the cation.

10 Such cocatalysts may be represented by the formula:



wherein: -

$L^*$  is a neutral Lewis base

$(L^*-H)_{+ci}$  is a Bronsted acid

15  $A^{d-}$  is a non-coordinating compatible anion having a charge of  $d-$ , and  
 $d$  is an integer from 1 to 3.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

20 Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic compounds used as cocatalysts are those wherein the cation of the ionic compound comprises a hydrocarbyl substituted ammonium salt and the anion  
25 comprises an aryl substituted borate.

Typical borates suitable as ionic compounds include:

triethylammonium tetraphenylborate

triethylammonium tetraphenylborate ,

tripropylammonium tetraphenylborate,

30 tri(n-butyl)ammonium tetraphenylborate,

tri(t-butyl)ammonium tetraphenylborate,

N,N-dimethylanilinium tetraphenylborate,

N,N-diethylanilinium tetrphenylborate,  
trimethylammonium tetrakis(pentafluorophenyl) borate,  
triethylammonium tetrakis(pentafluorophenyl) borate,  
tripropylammonium tetrakis(pentafluorophenyl) borate,  
5 tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,  
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

A preferred type of cocatalyst suitable for use with the metallocene complexes  
comprise ionic compounds comprising a cation and an anion wherein the anion has at least  
10 one substituent comprising a moiety having an active hydrogen.

Suitable cocatalysts of this type are described in WO 98/271 19 the relevant  
portions of which are incorporated herein by reference.

Examples of this type of anion include:

triphenyl(hydroxyphenyl) borate  
15 tri (p-tolyl)(hydroxyphenyl) borate  
tris (pentafluorophenyl)(hydroxyphenyl) borate  
tris (pentafluorophenyl)(4-hydroxyphenyl) borate

Examples of suitable cations for this type of cocatalyst include triethylammonium,  
triisopropylammonium, diethylmethylammonium, dibutylethylammonium and similar.

20 Particularly suitable are those cations having longer alkyl chains such as  
dihexyldecylmethylammonium, dioctadecylmethylammonium,  
ditetradecylmethylammonium, bis(hydrogenated tallow alkyl) methylammonium  
and similar.

Particular preferred cocatalysts of this type are alkylammonium  
25 tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred  
cocatalyst is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-  
hydroxyphenyl) borate.

With respect to this type of cocatalyst , a preferred compound is the reaction  
product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an  
30 organometallic compound, for example triethylaluminium or an aluminoxane such as  
tetraisobutylaluminoxane.

The catalysts used to prepare the novel copolymers of the present invention may suitably be supported.

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used for example polyethylene, polypropylene, clays, zeolites,  
5 etc.

The most preferred support material for use with the supported catalysts according to the method of the present invention is silica. Suitable supports are silicas having a median diameter (d50) from 20 to 70  $\mu\text{m}$ , preferably from 30 to 60  $\mu\text{m}$ . Particularly suitable supports of this type are Grace Davison D948 or Sylopol 2408 silicas as well as  
10 PQ Corporation ES70 or ES757 silica.

The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to  
15 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

The porous supports are preferably pretreated with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a  
20 temperature of -20°C to 150°C and preferably at 20°C to 100°C.

Particularly suitable catalysts for use in the preparation of the polyethylene powders of the present invention are metallocene complexes which have been treated with polymerisable monomers. Our earlier applications WO 04/020487 and WO 05/019275 describe supported catalyst compositions wherein a polymerisable monomer is used in the  
25 catalyst preparation. Polymerisable monomers suitable for use in this aspect of the present invention include ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, styrene, butadiene, and polar monomers for example vinyl acetate, methyl methacrylate, etc. Preferred monomers are those having 2 to 10 carbon atoms in particular ethylene, propylene, 1-butene or 1-hexene. Alternatively a combination of one or more monomers  
30 may be used for example ethylene/ 1-hexene. The preferred polymerisable monomer is 1-hexene.

The polymerisable monomer is suitably used in liquid form or alternatively may be used in a suitable solvent. Suitable solvents include for example heptane.

The polymerisable monomer may be added to the cocatalyst before addition of the metallocene complex or alternatively the complex may be pretreated with the  
5 polymerisable monomer.

The novel copolymers of the present invention may suitably be prepared in processes performed in either the slurry or the gas phase.

A slurry process typically uses an inert hydrocarbon diluent and temperatures from about 0°C up to a temperature just below the temperature at which the resulting polymer  
10 becomes substantially soluble in the inert polymerisation medium. Suitable diluents include toluene or alkanes such as hexane, propane or isobutane. Preferred temperatures are from about 30°C up to about 200°C but preferably from about 60°C to 100°C. Loop reactors are widely used in slurry polymerisation processes.

The novel copolymers are most suitably prepared in a gas phase process. Gas phase  
15 processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and  $\alpha$ -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art.

Typical operating conditions for the gas phase are from 20°C to 100°C and most preferably from 40°C to 85°C with pressures from sub-atmospheric to 100 bar.

20 Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 A and EP 6992 13A, with the latter being a particularly preferred process.

The low density polyethylene polymers (LDPE) of component (b) of the polymer blends of the present invention may be prepared by methods well known in the art, for  
25 example be prepared by use of conventional autoclave high pressure technology or by tubular reactor technology. The autoclave high pressure technology is preferred.

The LDPE may be a homopolymer of ethylene or a copolymer of ethylene and comonomers which include polar vinyl, conjugated and non-conjugated dienes, vinyl acids, vinyl esters, vinyl silanes, and the like. The LDPE may also comprise terpolymers.  
30 The most preferred LDPEs are homopolymers.

Use of the novel blends of the present invention leads to lower extrusion pressures as well as a reduction in the motor load and energy consumption even for those blends

containing a low amount of the LDPE component. The selection of the LLDPE component also brings additional energy savings compared with prior art LLDPEs. The higher melt strengths of the LDPE component also leads to improvements in film processability, improved bubble stability as well as higher extrusion rates.

5 According to another aspect of the present invention there is provided a polymer blend comprising 3 % - 10% by weight of an LDPE, said blend having:

- (i) Melt elasticity at 190°C,  $G'(G''=500 \text{ Pa}) \leq 110 \text{ Pa}$ , preferably in the range 40 - 80 Pa and more preferably in the range 40 - 70 Pa,
- (ii) Melt strengths at  $100 \text{ s}^{-1}$  shear rate at 190°C,  $MS(100 \text{ s}^{-1}) \geq 4.8 \text{ cN}$ ,  
 10 preferably in the range 5.6 - 9.0 cN and more preferably in the range 5.7 - 8.0 cN, and
- (iii) Melt Strength shear rate derivative at 190°C,  $5(MS)/5(\log \dot{\gamma}) \geq 5 \text{ cN}$ ,  
 preferably in the range 5.0 - 7.0 cN, and

The polymer blends of the present invention may be used for applications well  
 15 known in the art for example films.

Films may be formed by conventional extrusion processes for example film blowing, film casting or film lamination. The blends of the present invention are particularly advantageous for blown film extrusion processes. The polymer blends may be used as components of monolayer or multilayer films.

20 Thus according to another aspect of the present invention there is provided a film comprising a polymer blend as hereinbefore described.

In particular the present invention further comprises a film comprising a polymer blend comprising

- (a) 90 - 97% by weight of a copolymer of ethylene and an alpha olefin having from 3 to 10  
 25 carbon atoms, said copolymer having
  - (i) a density in the range 0.910 to 0.940  $\text{g cm}^{-3}$ ,
  - (ii) a melt index (190°C/2,16kg),  $MI_2 < 5$ , and
  - (iii) molecular weight distribution ( $M_{w-c} M_{n-c}$ , by classical GPC) in the range 2.0 - 5.0, and
- 30 (b) from 3 - 10% by weight of a low density polyethylene polymer having
  - (i) a density from 0.910 to 0.920  $\text{g cm}^{-3}$  and
  - (ii) a melt index (190°C/2, 16kg),  $MI_2 > 2$ , and



(iii) a melt elastic modulus  $G'(G'' = 500 \text{ Pa}) \geq 140 \text{ Pa}$  at  $190^\circ\text{C}$ .

wherein the sum of (a) and (b) is 100%.

The films thus obtained from the blend of LLDPE component (a) and LDPE component (b) have mechanical properties (Dart Drop Impact strength, MD Tear strength, puncture resistance) of at least 50%, preferably in the range 60 - 95%, and more preferably in the range 70 - 90 % of those obtained on similar film blown with the pure (unblended) LLDPE component (a). The films exhibit improved optical properties in particular when the LDPE component is present in lower amounts. Improved tear resistance in transverse direction and increase shrinkage may be observed the latter to the benefit of shrink film applications.

The extrudability of the films of the present invention is characterised by an Energy Index that is at least 5%, preferably in the range 5 - 11% and more preferably in the range 6 -10%, lower than the original (or unblended component (a)) polymer during blown film extrusion process. This is particularly applicable to blends where the copolymer of component (a) has a density in the range  $0.916$  to  $0.926 \text{ g cm}^{-3}$ .

Moreover, the films can be extruded at higher temperature and low frostline height with the addition of LDPE according to the invention at a concentration as low as 5 wt%.

The present invention will now be illustrated with reference to the following examples.

#### **Methods of test (polymers)**

Melt index:  $MI_2$  ( $190^\circ\text{C}/2.16 \text{ kg}$ ) and HLMI ( $190^\circ\text{C}/21.6 \text{ kg}$ ) were measured in accordance with the procedures of ISO 1133 at  $190^\circ\text{C}$  using loads of 2.16 kg and 21.6 kg, respectively.

Density of the polyethylene was measured according to ISO 1183-1 (Method A) and the sample plaque was prepared according to ASTM D4703 (Condition C) where it was cooled under pressure at a cooling rate of  $15^\circ\text{C}/\text{min}$  from  $190^\circ\text{C}$  to  $40^\circ\text{C}$ .

Dynamic rheological measurements are carried out, according to ASTM D 4440, on a dynamic rheometer (e.g., ARES) with 25 mm diameter parallel plates in a dynamic mode under an inert atmosphere. For all experiments, the rheometer has been thermally stable at  $190^\circ\text{C}$  for at least 30 minutes before inserting the appropriately stabilised (with anti-oxidant additives), compression-moulded sample onto the parallel plates. The plates are then closed with a positive normal force registered on the meter to ensure good contact.

After about 5 minutes at 190°C, the plates are lightly compressed and the surplus polymer at the circumference of the plates is trimmed. A further 10 minutes is allowed for thermal stability and for the normal force to decrease back to zero. That is, all measurements are carried out after the samples have been equilibrated at 190°C for about 15 minutes and are run under full nitrogen blanketing.

Two strain sweep (SS) experiments are initially carried out at 190°C to determine the linear viscoelastic strain that would generate a torque signal which is greater than 10% of the lower scale of the transducer, over the full frequency (e.g. 0.01 to 100 rad/s) range. The first SS experiment is carried out with a low applied frequency of 0.1 rad/s. This test is used to determine the sensitivity of the torque at low frequency. The second SS experiment is carried out with a high applied frequency of 100 rad/s. This is to ensure that the selected applied strain is well within the linear viscoelastic region of the polymer so that the oscillatory rheological measurements do not induce structural changes to the polymer during testing. In addition, a time sweep (TS) experiment is carried out with a low applied frequency of 0.1 rad/s at the selected strain (as determined by the SS experiments) to check the stability of the sample during testing.

#### Measurement of Melt Elastic Modulus $G'(G''=500 \text{ Pa})$ at 190°C:

The frequency sweep (FS) experiment is then carried out at 190°C using the above appropriately selected strain level and the dynamic rheological data thus measured are then analysed using the rheometer software (viz., Rheometrics RHIOS V4.4 or Orchestrator Software) to determine the melt elastic modulus  $G'(G'' = 500 \text{ Pa})$  at a constant, reference value (500 Pa) of melt viscous modulus ( $G''$ ).

#### Flow Activation Energy ( $E_a$ ) Measurement

The bulk dynamic rheological properties (e.g.,  $G'$ ,  $G''$  and  $\eta^*$ ) of all the polymers were then measured at 170°, 190° and 210°C. At each temperature, scans were performed as a function of angular shear frequency (from 100 to 0.01 rad/s) at a constant shear strain appropriately determined by the above procedure.

The dynamic rheological data was then analysed using the Rheometrics Software (TA Orchestrator). The following conditions were selected for the time-temperature (t-T) superposition and the determination of the flow activation energies ( $E_a$ ) at 190°C

according to an Arrhenius equation,  $a_T = \exp(E_a/kT)$ , which relates the shift factor ( $a_T$ ) to  $E_a$ :

	Rheological Parameters:	$G'(co), G''(co) \text{ \& } \eta^*(\omega)$
	Reference Temperature:	190°C
5	Shift Method:	2D (i.e., horizontal & vertical shifts) Minimisation
	Calculation Method:	Residual Minimisation
	Shift Accuracy:	High
	Interpolation Mode:	Cubic Spline

#### 10 Rheotens Extensional Rheometry

The melt strength of the polymer is measured at 190°C, using a GottfertRheotens extensional rheometer placed beneath a GottfertRheotester 2000 Capillary Rheometer (12 mm barrel diameter). This is achieved by extruding the polymer at a constant pressure (P) through a die of 1.5 mm diameter and 30 mm in length, with a 90° entry angle. The spin-  
15 line length (L) distance between die exit and the centre of the upper wheels is fixed at 101 mm.

Once an extrusion pressure is selected, the piston of the capillary rheometer will travel through its 12 mm diameter barrel at a speed that is sufficient to maintain that pressure constant using the constant pressure system of the rheometer. The nominal wall  
20 shear rate ( $\dot{\gamma}$ ) for a given extrusion pressure can then be computed for the polymer at the selected pressure.

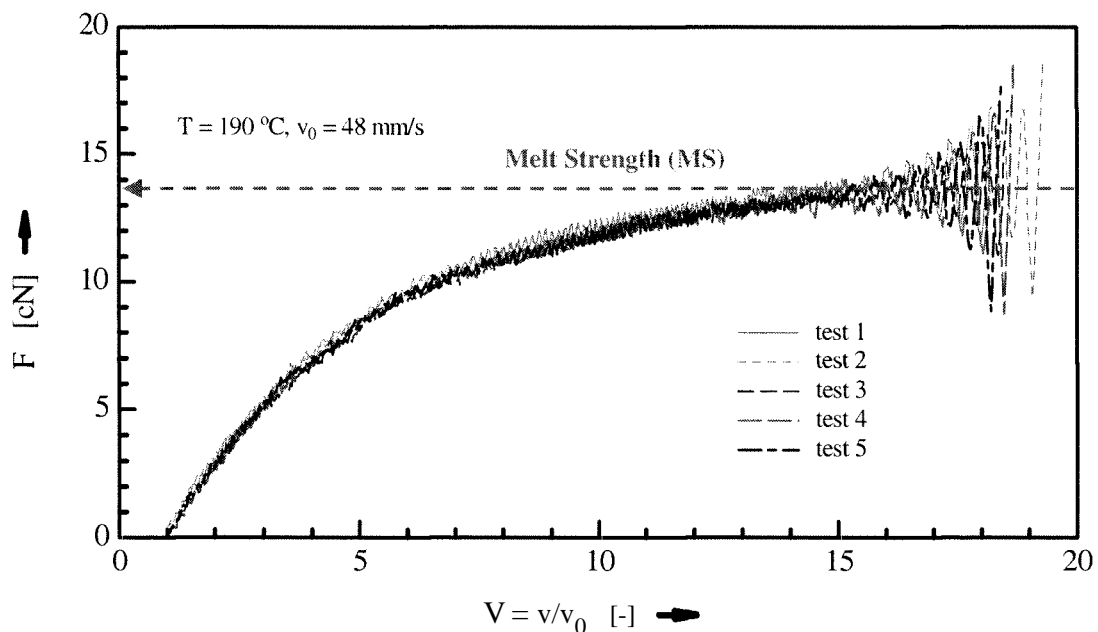
In a Rheotens test, the polymer strand is extruded continuously at a given extrusion pressure and it is taken up by the Rheotens wheels after a spin-line length L, where the wheels turn with a steadily increasing velocity v and draw down the polymer strand. The  
25 resistance of the material against this drawdown is then measured by a force balance in the arm onto which the wheels are fixed.

At the start of the experiment, the velocity of the Rheotens wheels is adjusted in such a way that it is equal to the actual velocity relative to the strand. Therefore, if a material exhibits extrudate swell at the die exit,  $v_s$  is smaller than the extrusion velocity  $v_s^{3/4}$   
30 calculated from volumetric output, density and the die diameter. The signal of the force

balance of the transducer is equal to zero at the starting point, as the material is not yet elongated.

The force signal can be calibrated with defined weights as described in the manufacturer (Gottfert) document and procedure. The resulting force signal  $F$  is measured until rupture of the strand. The maximum force at rupture is also referred to as melt strength (MS), while the maximum velocity is called drawability of the melt.

Melt strength measurements are often confronted with a melt resonance, which is hydrodynamic instability that is reflected by growing oscillations in force as the elongation proceeds. It is known to those of ordinary skill in the art that the melt strength (MS) of a sample exhibiting melt resonance can be obtained by fitting a best line to the Rheotens Force - Velocity ( $F - v$ ) curve from the initial non-resonated region through the mid-point of the oscillating peaks (of increasing amplitude as elongation proceeds) along the resonance region until the point of rupture (See Figure).



Once a constant pressure is attained after launching the piston of the capillary rheometer, the zero of the Rheotens instrument is set in the software; the strand is cut and clamped between the upper rotating wheels.

The initial wheel velocity is chosen so as to guide the extruded strand, i.e. at zero force. In practice it is preferably to starting the test at slightly higher velocities in order to achieve a better clamping of the strand when it starts thinning and enabling one to reach higher velocities without problems.

In principle, there is an effect of the weight of the strand below the Rheotens on the force measurement. To alleviate this effect the strand is manually guided once it reaches the table (~ 360 mm below the wheels).

The extrudate can be drawn with a pair of gear wheels at accelerating speed ( $v$ ) range of (3 - 24 mm/s<sup>2</sup>). Lower velocities give the best resolution but a higher acceleration can be useful to postpone the instability. Typical acceleration of 3 mm/s<sup>2</sup> was used when tested at 190°C. The drawing force ( $F$ ) experienced by the extrudate is measured with a transducer (appropriately calibrated in accordance with the manufacturer (Gottfert) recommended procedures) and recorded accordingly together with the drawing speed. The maximum force at break is defined as melt strength (**MS**) at a constant extrusion pressure ( $P$ ) or at its corresponding extrusion rate ( $\dot{\gamma}$ ). Three or four extrusion pressures are typically selected (6, 8, 12, 16 MPa) for each polymer depending on its flow properties. For each extrusion pressure, a minimum of 3 MS measurements are performed and an average MS value is then obtained.

The derivative functions of the extrusion pressure and shear rate dependent melt strengths,  $\delta(\mathbf{MS})/\delta(P)$  and  $\delta(\mathbf{MS})/\delta(\log \dot{\gamma})$ , for each polymer are computed from the slopes of the plots of the average **MS** against the extrusion pressure ( $P$ ) and against the logarithm of the shear rate ( $\log \dot{\gamma}$ ), by linear and natural logarithmic regression respectively. The melt strength at shear rate of 100 s<sup>-1</sup>, **MS**(100 s<sup>-1</sup>), can also be computed from the natural logarithmic (Ln) trend/regression of the MS vs. ( $\log \dot{\gamma}$ ) plot: i.e.,

$$\mathbf{MS}(\dot{\gamma}) = m \ln(\dot{\gamma}) + C$$

where  $\delta(\mathbf{MS})/\delta(\log \dot{\gamma}) = 2.303 \times m$ , and  $\mathbf{MS}(100 \text{ s}^{-1}) = m \ln(100) + C$

#### High Temperature Gel Permeation (Size Exclusion) Chromatography Analysis

The molecular structures of the polymers were characterized using two independent systems of High Temperature Gel Permeation (or Size Exclusion) Chromatography Analysis: (i) A route classical GPC by conventional polystyrene (PS) calibration method for apparent molecular weight distribution (e.g., number average,  $M_{n,cc}$ , and weight average molar mass,  $M_{w,cc}$ , values) determination and (ii) A Multi-Angle Laser Light Scattering apparatus (SEC/MALLS) for Absolute Molecular Weight Distribution (e.g., number average,  $M_{n,LS}$ , and weight average molar mass,  $M_{w,LS}$ ) determination, as well as

the apparent molecular weight distribution by conventional PS calibration (e.g., number average,  $M_{n,calc}$ , and weight average molar mass,  $M_{w,calc}$ ) determination. Hence, there are two set of apparent molecular weights parameters appropriately labelled in accordance with their GPC systems thus employed.

5 High Temperature Gel Permeation (Size Exclusion) Chromatography Analysis by Calibration (Classical GPC) for Apparent Molecular Weight Distribution Determination

Apparent molecular weight distribution and associated averages, uncorrected for long chain branching, were determined by Gel Permeation (or Size Exclusion) Chromatography according to ISO16014-1, ISO 16014-2 and 16014-4, using a PL 220 of Polymer

- 10 Laboratories with 4 WATERS STYRAGEL HMW 6E columns of 30 cm in length and 1 Waters Styragel 4.6 x 30 mm guard column and a differential refractometer detector. The solvent used was 1,2,4 Trichlorobenzene at 150°C, which is stabilised with BHT, of 0.2 g/litre concentration and filtered with a 0.45 µm Osmonics Inc. silver filter. Polymer solutions of 0.8 g/litre concentration were prepared at 160°C for one hour with stirring only
- 15 at the last 30 minutes. The nominal injection volume was set at 400 µl and the nominal flow rate was 1 ml/min.

A relative calibration was constructed using 13 narrow molecular weight linear polystyrene standards:

PS Standard	Molecular Weight
1	7 520 000
2	4 290 000
3	2 630 000
4	1 270 000
5	706 000
6	355 000
7	190 000
8	114 000
9	43 700
10	18 600
11	10 900
12	6 520
13	2 950

The elution volume,  $V$ , was recorded for each PS standards. The PS molecular weight was then converted to PE equivalent using the following Mark Houwink parameters

$k_{pS} = 1.21 \times 10^{-4} \text{ dl.g}^{-1}$ ,  $\alpha_{pS} = 0.707$ ,  $k_{pe} = 4.06 \times 10^{-4} \text{ dl.g}^{-1}$ ,  $\alpha_{pe} = 0.725$ . The calibration curve  $Mw_{PE} = f(V)$  was then fitted with a first order linear equation. All the calculations are done with Empower 2 software from Waters.

5 High Temperature Gel Permeation (Size Exclusion) Chromatography Analysis coupled with a High Temperature Multi-Angle Laser Light Scattering apparatus (SEC/MALLS) for Absolute Molecular Weight Distribution Determination

The measurements were carried out in a high temperature GPC (PL 220, Varian Inc.) with an on-board differential refractometer. It is coupled with a high temperature multi-  
10 angle laser light scattering apparatus (MALLS, Dawn EOS, Wyatt Technologies). The measuring temperature was  $140^{\circ}\text{C}$ , for both the sample and the column compartments, and 1,2,4 trichlorobenzene was used as solvent which was distilled in vacuum at a pressure of  $10^{-2}$  mbar or better prior to use. The temperature was calibrated by thermocouples in the sample and the carousel compartment. The solvent was degassed using the on-board  
15 degasser of the PL 220. The flow rate was chosen to 0.5 ml/min and 200  $\mu\text{l}$  of the polymer solution was injected onto the column system consisting of three columns Shodex UT806M (Showa Denko, exclusion limit determined for polystyrene molar mass  $5 \times 10^7$  g/mol) and one high molar mass separation column Shodex UT807 (exclusion limit  $2 \times 10^8$  g/mol). The concentration of the polymer eluted from the columns was measured by means  
20 of two concentration detectors using different detection techniques (infra red absorption, polyCHAR IR4, and a differential refractive index detector, an internal detector of the PL 220). Data were collected and processed using the Wyatt Astra software 4.73. All 18 angles of the MALLS were used to evaluate the data.

Solutions of the polymers were prepared in individual sample vials as follows: about  
25 12 mg of polymer was weighed out into the vial and 4 ml of 1,2,4-trichlorobenzene (TCB), stabilized with 0.1 weight% Irganox 1035 was added. The samples were allowed to dissolve for three hours at  $160^{\circ}\text{C}$ . The solution process was supported by slight agitation by hand. Samples were not filtered. After the dissolution which is controlled by a visual inspection, the solutions are transferred into preheated measuring vials of 2ml content and  
30 placed into the auto-sampler of the HT-GPC apparatus. Two injects from individual vials (duration of collection run of 105 min each) from each solution were performed to assure reproducibility, which was verified by using the raw signal of the MALLS and the

concentration signal from the IR-detector. In addition, no significant influence of the residence time in the HT-GPC apparatus was found (indicating no polymer degradation) for all the measurements.

The mass recovery,  $r$ , from the columns is being defined by integration of the concentration signal as follows

$$r = \frac{m_{\text{detected}}}{m_{\text{injected}}} \cdot 100\%$$

Comparing the detected mass  $m_{\text{detected}}$  with the injected mass  $m_{\text{injected}}$  it can be used to evaluate how large the amount of gels/insoluble material is or if material is being absorbed on the columns.

The mass recovery is around 90% or larger for all samples measured. In routine measurements values of 90 % and more are typical and indicate that all dissolved material is eluted from the columns and that no gels are present.

A similar value is found for a narrow molar mass distribution ( $M_{w,LS} = 200$  kg/mol,  $M_{z,LS} = 375$  kg/mol and  $M_{w,LS}/M_{n,calib} = 2$ ) linear homo-polyethylene sample from the IUPAC Working Party IV 2.2, Project Subgroup 5 (thus referred as IUPAC 5A linear standard, that was previously used and published in a paper by Claus Gabriel, Esa Kokko, Barbro Lofgren, Jukka Seppala, Helmut Miinstedt, "Analytical and Rheological Characterization of Long-Chain Branched Metallocene-catalyzed Ethylene Homopolymers", Polymer **43** (2002) 6383-6390).

Designation	$M_{w,LS}$ , kg/mol (absolute)	$M_{w,calib}$ , kg/mol (from calibration)	$M_{n,calib}$ , kg/mol (from calibration)	$M_{w,LS}/M_{n,calib}$
IUPAC 5A	200±3	200±1	100±2	2.0±0.1

The radii of gyration for polyethylene IUPAC 5A show the behaviour of linear polymers, with an average value  $\langle r_g^2 \rangle^{0.5}$  of 45.6 nm, and can be described by a power-law with an exponent of 0.58 [T. Sun, P. Brant, R.R. Chance, W.W. Graessley, "Effect of Short Chain Branching on the Coil Dimensions of Polyolefins in Dilute Solution", Macromolecules **34** (2001) 6812 - 6820] which is in agreement with literature (P. Tackx and J.C.J.F Tacx, Polymer **39** (1998) 3109 - 3113).

The data collection and the evaluation of the measurements were performed under ASTRA 4.73 (Wyatt Technologies). The concentration signal from the IR-detector was



used in the evaluation of the data because of its higher sensitivity. The determination of the absolute molar mass and of the radius of gyration  $\langle r_g^2 \rangle^{0.5}$  for each fraction eluted was done in a linear Zimm-plot. In parallel the same concentration signal was collected and evaluated via the calibration curve connecting elution volume with the molar mass of polymer standards using the WinGPC 6.20 software (Polymer Standard Services).

The GPC was calibrated with 13 polystyrenes standards of Polymer Laboratories, with narrow molar mass distribution characterized by  $M_w/M_n$ -values below 1.1. The calibration curve spans a molar mass range from 0.58 kg/mol to 11600 kg/mol, with the individual molar masses at 11600, 7300, 2750, 1750, 900, 490, 230, 70.95, 30.0, 10.68, 3.95, 1.3, and 0.58 kg/mol.

The standards were measured in three batches. The Table below gives the combinations and the concentrations of the standards used. The standards were dissolved in about 7 ml TCB using the dissolution method similar to that of the polyethylene samples except that the dissolution time was only 60 minutes. The chromatographic concentrations thus used were low enough to eliminate the concentration effects on molecular weight (the 2<sup>nd</sup> virial coefficient effects).

**Designation of the calibration batches**

	Standard, [kg/mol]	Concentration, [mg/ml]
Batch 1	11600	0.5
	1750	0.75
	230	1.5
	10.68	2.5
	0.58	3.0
Batch 2	2750	0.5
	490	0.75
	30	1.5
	3.95	3.0
Batch 3	7300	0.5
	900	0.75
	70.95	1.5
	1.3	3.0

For the measurements of polyethylene samples the polystyrene calibration was converted into a polyethylene calibration using the universal calibration technique. The following Mark Houwink parameters,  $k_{ps} = 1.21 \times 10^{-4} \text{ dl.g}^{-1}$ ,  $\alpha_{ps} = 0.707$ ;  $k_{pe} = 4.06 \times 10^{-4} \text{ dl.g}^{-1}$ ,  $\alpha_{pe} = 0.725$  were used to correct for the different hydrodynamic volumes of polystyrene and polyethylene in solution. The refractive index concentration coefficient,  $dn/dc$ , of  $0.104 \text{ ml.g}^{-1}$  has been used. All chromatograms were corrected with respect to the elution volume of the internal standard.

The multi-detector offsets were determined using a narrowly distributed PS ( $M=30.000 \text{ g/mol}$ ), according to Method 1 described in *"Data Interpretation For Coupled Molecular-Weight Sensitive Detectors In SEC - Interdetector Transport Time"* by P. Cheung, St. Balke and Th. Mourey, (published by Journal Of Liquid Chromatography, 15(1) (1992) 39-69, DOI: 10.1080/10826079208018808). It is performed as follows (feature of the ASTRA software):

The peaks of the IR and RI detector are shifted along the retention volume axis until the Peak maximum and the rising flank of the peak coincide with peak of the MALLS  $90^\circ$  detector. The shift in volume between the detectors is stored in the software.

The SEC/MALLS system yields sample bulk absolute number average ( $M_n$ ) and weight average molar mass ( $M_w$ ) values (namely,  $M_{w-Ls}$  and  $M_{n-Ls}$ ) from the MALLS apparatus, and with the conventional universal calibration method produces also the corresponding apparent values (namely,  $M_{w-c_{aib}}$  and  $M_{n-c_{aib}}$ ). The determination of the radius of gyration  $\langle r_g^2 \rangle^{0.5}$  for each fraction eluted was also done in a linear Zimm-plot.

The branching in the polymer can be evaluated from the comparison of the mean square radius of gyration of the sample,  $[\langle r_g^2 \rangle]_{br}$ , against that of the IUPAC 5A linear standard,  $[\langle r_g^2 \rangle]_{lin}$ , for each fraction (i.e., at the same molecular weight), yielding the branching index (or contraction) factor,  $g$ , of the sample (B.H.M. Zimm, W.H. Stockmayer, *"The Dimensions of Molecules Containing Branching and Rings"*, J. Chem. Phys. 17(12) (1949) 1301 - 1314):

$$g = \frac{\langle r_g^2 \rangle_{br}}{\langle r_g^2 \rangle_{lin}}$$

For short and long-branched molecules, a contraction of the coils in solution with  $g < 1$  is typically observed. The number of branches per molecule, or the average number of branches per 1000 monomers, can also be calculated from the  $g$  ratio.

5            Although the melt rheology of a polymer does not appear to be significantly affected by the presence of short chain branching (SCB), the latter does influence the size-mass relationship and hence on the characterization of MWD and long chain branching (LCB) using SEC/MALLS, [for example, see T. Sun, P. Brant, R.R. Chance, W.W. Graessley, "*Effect of Short Chain Branching on the Coil Dimensions of Polyolefins in*  
10   *Dilute Solution*", *Macromolecules* **34** (2001) 6812 - 6820].

The amounts of short and long branching each contribute to the branching index have been described in the literature by the formula:

$$g = g_{LCB} \times g_{SCB},$$

and there are few reliable theoretical relationships between the radius of gyration ( $r_g$ ) and  
15   the short chain branching (SCB) content due to the complex relationship and interaction of the polymer dimension with its environments (e.g., polymer chains - solvent interaction, 'goodness' of solvent, etc). The correction of SCB effect on  $r_g$  has often been done empirically [for example, see Youlu Yu *et al*, *Polymer* **46** (2005) 5165 - 5182), and T. Sun, P. Brant, R.R. Chance, W.W. Graessley, "*Effect of Short Chain Branching on the Coil*  
20   *Dimensions of Polyolefins in Dilute Solution*", *Macromolecules* **34** (2001) 6812 - 6820].

The literature study of Sun *et al* on the size - mass contribution of SCB has shown that the short chain branching index or SCB contraction factor,  $g_{SCB}$ , of 4 series of copolymers of ethylene ( $M_w/M_n \sim 1.89 - 4.26$ , with propylene, 1-butene, 1-hexene and 1-octene) varies linearly with comonomer weight fraction, with slope that depends on the  
25   comonomer type. For example, in the case of 1-hexene copolymers of ethylene, Tables 1 and 4 of Sun *et al* publication yielded a linear relationship (with a coefficient of correlation or determination,  $R^2 = 0.997$ ) between the average SCB branching index ( $g_{SCB}$ ) with the weight fraction (in %) of 1-hexene in the copolymers, as described by the following equation:

$$g_{SCB} = -0.0058 \times [EH] + 0.9771,$$

where [EH] is the weight fraction (wt %) of 1-hexene in the copolymers of ethylene.

Accordingly, for hexene-copolymers of ethylene in the similar range of  $M_w/M_n$ , one may empirically and approximately correct the SCB effect using the above equation to obtain an average branching index predominantly (if not completely) due to long chain branching, i.e.,  $g_{corrected} \cong g_{LCB}$ , for the case where the SEC/MALLS experimental set up does not have an additional IR detector for simultaneous FTIR - SCB measurements, and/or have suitable set of SCB PE standards for calibration.

The indicative of the presence of long chain branching (LCB) in the polymer can also be observed from the differences (or the ratio,  $M_{wLS}/M_{wcalib}$ ) between the absolute weight-average molecular weight ( $M_{wLS}$ ), as measured by the MALLS apparatus, and the apparent weight-average molecular weight ( $M_{wcalib}$ ), obtained by the conventional calibration route, using the same SEC/MALLS system during the same run.

#### Film Characteristics

Prior to testing, all the films were stored in a conditioned room (23 °C, 50 % humidity) for at least 40 hours after extrusion.

Dart Drop Impact strength (DDI) was measured by ISO 7765-1 (1988) (Method A), using a Tufnol (Carp Brand to BS.6128) 70g Dart Head and the diameter of the incremental weights is equal to the diameter of the dart head (38.1 mm).

Haze by ASTM D 1003-92 and Gloss (45°) by ASTM D2457-90.

Tear strength (Elmendorf) in machine (MD) and transverse (TD) directions by ASTM D1922-93.

Tensile properties (500 mm/min) and secant modulus (1%, 5 mm/min) were measured on a Zwick 1445 equipment with a load cell of 1000 N according to ISO 527-1&3 (1995). Five distinct film specimens (type 2) were measured both in MD and TD directions, and the average value is reported.

Shrinkage measurements in MD and TD directions according to ISO 14616 (1997) were performed after conditioning in an oven at 160°C for blended materials containing mLLDPE partner with a density lower than 922 kg/m<sup>3</sup>, or 170°C for blended materials containing mLLDPE partner with a density higher than 925 kg/m<sup>3</sup>.

**Examples - LLDPE components I - IX**

LLDPE components I to VI were prepared by the copolymerisation of ethylene with 1-hexene in a gas phase fluidized bed reactor under the general process settings disclosed in WO 06/085051 in the presence of the constrained geometry catalyst disclosed in WO 2010/000557. The details of the polymerisation conditions are summarized in Table 1

**TABLE 1**

		I	II	III	IV	V	VI
Reactor diameter	m	5	5	5	0.74	5	0.74
Temperature	°C	80	80	82	80	80	76
Bed height	M	15.2	15.2	15.2	6.0	15.2	5,8
Ethylene partial pressure	Bar	12.0	12.0	12.0	13.2	11.5	12.5
Hydrogen/ethylene ratio	bar/bar	0.0031	0.0039	0.0027	0.0025	0.0027	0.0028
Hexene/ethylene ratio*	wt%	8.8	9.3	5.8	7.6	9.6	10.5
Pentane partial pressure	Bar	2.4	2.4	3.2	2.9	1.5	2.3
Residence time	h	5	5	5	4.1	6.5	3.7
Space time yield	kg/h/m <sup>3</sup>	72	72	60	84	55	80

\*ratio based on the mass flow-rates of hexene and ethylene to the reactor

LLDPE components VII, VIII and IX are metallocene-based polyethylenes available from ExxonMobil Chemical Company under the trade names Exceed™ 1018-CA, Enable™ 20-05 CH and Enable™ 27-05 CH, respectively. It is known from public available information (e.g. WO 2009/109367) that Exceed™ grades are linear metallocene polyethylenes substantially free of long chain branching obtained in a gas phase process using a non-bridged bis-cyclopentadienyl zirconocene transition metal component, while Enable™ grades are homogeneously branched long-chain branched linear polyethylenes obtained in a gas phase process using a supported catalyst with a bridged bis-indenyl zirconocene complex

**TABLE 2**

LLDPE	I	II	III	IV	V	VI	VII	VIII	IX
Density (g/cm <sup>3</sup> )	0.9177	0.9171	0.9256	0.9183	0.9181	0.9127	0.9185	0.9202	0.9273
Hexene Content (wt %)	7.9	8.7	5.4	8.3	8.0	12.0	n.a.	n.a.	n.a.
MI <sub>2</sub> (190°C, g/10min)	1.29	2.08	1.35	0.8	0.95	0.83	1.10	0.50	0.44
HLM <sub>I</sub> (190°C, g/10min)	25.2	40.5	28.7	13		16.3	16.1	20	21.0
HLM <sub>I</sub> /MI <sub>2</sub> (= MIR)	19.5	19.5	21.2	22.0		19.6	14.6	40	47.7
G'(G''=500Pa), (190°C, Pa)	44	30	55	58	64	33	8	116	123
Ea (kJ/mol) 190°C	32.2	32.3	32	31.7		32	30.5	56	68,7
Melt Strength at 100 s <sup>-1</sup> shear rate, <b>MS</b> (100 s <sup>-1</sup> ), (190°C, cN)	3.6	2.2		5.1		3.9	3.7	5.6	4.5
Melt Strength shear rate derivative, $\delta(\mathbf{MS})/\delta(\log \dot{\gamma})$ , (190°C, cN)	3.92	1.83		4.06		3.08	4.31	4.79	3.40
Melt Strength pressure derivative, $\delta(\mathbf{MS})/\delta(\mathbf{P})$ , (190°C, cN/MPa)	0.232	0.12		0.195		0.18	0.13	0.367	0.252
M <sub>w-cc</sub> (kDa) (classical)	120	111	123	136	115	129	136	116	121
M <sub>w-cc</sub> /M <sub>n-cc</sub> (classical)	3.7	3.7	4.2	3.7	3.8	3.2	2.8	3.3	3.8
M <sub>w-LS</sub> /M <sub>n-calib</sub> (SEC/MALLS)*	3.4				4.3				
M <sub>w-LS</sub> /M <sub>w-calib</sub> (SEC/MALLS)*	0.98				1.04				
$\langle r_g^2 \rangle^{0.5}$ , (nm)	30				51				
Branching Index, or Contraction Factor <sup>***</sup> , g	0.92				0.88				

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30

LLDPE	I	II	III	IV	V	VI	VII	VIII	IX
SCB Corrected Branching Index, or LCB Contraction Factor, $g_{corrected} \cong g_{LCB}$	0.99				0.95				
$M_{w-LS}$ (kDa) (SEC-MALLS)	109				117				

\*where  $M_{wLS}$  was measured by MALLS;  $M_{wcalib}$  and  $M_{n-calib}$  were measured by calibration using the same SEC/MALLS apparatus and experimental set-up as described (i.e., they were not measured by the classical GPC procedure).

\*\*\* numerical average

5

#### LDPE components A and B

LDPE components A and B were produced in a dual reactor high pressure DuPont autoclave polymerization process at an output rate of about 18 tons/hour. The typical polymerization conditions are summarized in Table 3 and polymer properties are shown in

10 Table 4.

**TABLE 3**

LDPE A		LDPE B	
<i>Reactor 1</i>		<i>Reactor 1</i>	
Temperature (°C)	250	Temperature (°C)	205
Pressure (bars)	1450	Pressure (bars)	1850
C <sub>2</sub> inlet temp (°C)	25	C <sub>2</sub> inlet temp (°C)	25
Residence time (s)	19	Residence time (s)	21
Peroxide	'Bu-peroxy-3,5,5-trimethyl hexanoate	Peroxide	'Bu-peroxy-2-ethyl hexanoate
Chain transfer agent	propylene	Chain transfer agent	propylene
<i>Reactor 2</i>		<i>Reactor 2</i>	
Temperature (°C)	250	Temperature (°C)	240
Pressure (bars)	1450	Pressure (bars)	1850
C <sub>2</sub> inlet temp (°C)	25	C <sub>2</sub> inlet temp (°C)	25
Residence time (s)	7	Residence time (s)	8
Peroxide	'Bu-peroxy-3,5,5-trimethyl hexanoate	Peroxide	'Bu-peroxy-3,5,5-trimethyl hexanoate
Chain transfer agent	propylene	Chain transfer agent	propylene



**TABLE 4**

LDPE	A	B
Density (g/cm <sup>3</sup> )	0.9162	0.9217
MI <sub>2</sub> (190°C, g/10 min)	3.7	1.4
HLMI (190°C, g/10 min)	146.2	76
HLMI/MI <sub>2</sub> (= MIR)	39.5	54.3
G'(G''=500Pa) (190°C, Pa)	153	104
Ea (kJ/mol) 190°C	50.1	68.5
Melt Strength at 100 s <sup>-1</sup> shear rate, <b>MS</b> (100 s <sup>-1</sup> ), (190°C, cN)	12.5	7.9
M <sub>n-cc</sub> (kDa)(classical)	22.5	25.5
M <sub>w-cc</sub> (kDa) (classical)	212	137
M <sub>z-cc</sub> (KDa)(classical)	802	458
M <sub>w-cc</sub> /M <sub>n-cc</sub> (classical)	9.4	5.4
M <sub>w-LS</sub> (kDa) (SEC-MALLS)*	850	210
Contraction Factor**, <b>g</b>	0.24	0.35
M <sub>w-LS</sub> /M <sub>n-Calib</sub> (SEC/MALLS)*	40.5	10.5
M <sub>w-LS</sub> /M <sub>w-calib</sub> (SEC/MALLS)*	3.35	1.72

\*where  $M_{w-LS}$  was measured by MALLS;  $M_{w-calib}$  and  $M_{n-calib}$  were measured by calibration  
5 using the same SEC/MALLS apparatus and experimental set-up as described (i.e., they were not measured by the classical GPC procedure).

\*\* numerical average

The following 2-component blends were prepared by combination of the above LLDPE copolymers and the low density polyethylenes (LDPE) fed to the extruder via two distinct feeders.

5 Blown film extrusion of mLLDPE-LDPE compositions

Monolayer films were extruded on a CMG 1200 TSA extruder provided by CostruzioniMeccaniche Gallia:

	Screw diameter	55 mm
10	Screw L/D ratio	30
	Die diameter/gap	150/2.2 mm
	Screen pack	flat

Extrusion conditions set up (unless otherwise stated):

15	Screw temperature profile	200/2 10/2 10/220/220°C
	Die temperature profile	220/220/220/220°C
	Output*(Q)	50 kg/h
	Take-off speed	30 m/min
	Blow-up ratio	2.5:1
20	Cooling air temperature	20°C
	Air blower adjustment	22 - 29% to maintain frostline height
	Frostline height	430 mm
	Film thickness	25 µm

(\*: The output rate, Q, and composition of the blends were measured by the actual weight variation on the feeders graduated with weight scales. The screw speed is automatically varied in order to achieve the required output rates.)

Further film extrusion conditions are shown in Table 5.

**TABLE 5- Film Extrusion of polymer blends**

Ex	LLDPE	LDPE	LLDPE/LDPE wt%/wt%	Melt Temp (°C)	Melt Pressure (bars)	Motor load /Amperage (A)	Screw speed (rpm)	Energy Index (rpm x A / Q)
CE1	I	A	98:2	217	213	83	51	84.8
2	I	A	95:5	217	213	81	51	82.6
3	I	A	93:7	216	206	80	51	81.1
4	I	A	90:10	217	210	79	51	80.6
CE 5	I	A	80:20	217	204	75	51	76.5
CE 6	I	none	100:0	217	213	85	52	88.4
CE 7	I	B	95:5	217	212	81	52	84.2
CE8	I	B	90:10	217	210	79	52	82.2
CE 9*	II	none	100:0	217	162	74	51	75.5
10	II	A	92:8	216	160	71	50	71.4
CE 11	III	none	100:0	217	205	80	52	83.2
12	III	A	95:5	216	201	76	51	77.5
13	III	A	90:10	217	195	73	51	74.5
CE 14	IV	none	100:0	217	270	88	61	107.0
15	IV	A	95:5	217	259	84	61	102.6
CE 16	VI	none	100:0	216	285	100	55	110.0
CE17 **	VII	none	100:0	198	292	91	58	105.6
18	VII	A	95:5	217	254	87	56	97.4
CE 19	VIII	none	100:0	212	232	74	59	87.3
CE 20	IX	none	100:0	217	226	79	58	91.6

\*: to achieve a good bubble stability, frostline height had to be increased up to 650 mm

5 (instead of 430 mm)

\*\*: extrusion was not possible under reference conditions. Extrusion temperature has been decreased down to 200°C (instead of 220°C).

It can be seen from Table 5 that the use of the novel blends of the present invention lower extrusion pressures as well as a reduction in the motor load and energy consumption (i.e., lower the Energy Index) may be observed even for those blends containing a low amount of the LDPE component (e.g., Ex 2 - 4 versus CE 1, for LLDPE I with LDPE A, and CE 6). The selection of the LLDPE component I - VI brings additional energy savings compared with LLDPEs VII - IX (i.e., CE 17, CE 19 and CE 20). The selection of the LDPE A leads to better improvements in extaidability, as compared to LDPE B during blown film extrusion (e.g., Ex 2 and Ex 4 blends, of 5% and 10% LDPE A with LLDPE I,

exhibit respectively lower Energy Indexes than those of corresponding CE 7 and CE 8 blends of LLDPE I with LDPE B at similar concentrations).

Moreover, the addition of LDPE A at a concentration as low as 5 wt% makes possible to extrude film at higher temperature and low frostline height (blend Ex 18 vs. CE 17 and blend Ex 10 vs. CE9).

**TABLE 6 - Properties of the polymer blends**

Ex	LLDPE	LDPE	LLDPE/ LDPE	G' (G''=500 Pa) (Pa)	Melt Strength at 100 s <sup>-1</sup> shear rate, MS(100 s <sup>-1</sup> ), (190°C, cN)	Melt Strength shear rate derivative, $\delta(\text{MS})/\delta(\log \dot{\gamma})$ , (190°C, cN)	Melt Strength pressure derivative, $\delta(\text{MS})/\delta(P)$ , (190°C, cN/MPa)	Ea (kJ/ mol)	Mw (kDa) classic al	Mw/M n classic al
CE1	I	A	98:2*	46*						
2	I	A	96:5*	50*					122*	3.8*
3	I	A	93:7*	53*						
4	I	A	90:10**	57	7.1	6.59	0.40			
CE5	I	A	80:20**	68	9.1	5.84	0.37			
CE 6	I	none	100:0	44	3.6	3.92	0.23	32.2	112	3.7
CE 7	I	B	95:5*	50*						
CE 8	I	B	90:10**	56	4.7	2.84	0.22			
CE 9	II	none	100:0	30				32.3	111	3.7
10	II	A	92:8*	42*						
CE 11	III	none	100:0	55				32.0	123	4.2
12	III	A	95:5**	60					126	4.5
13	III	A	90:10**	68					130	4.2
CE 14	IV	none	100:0	58	5.1	4.06	0.20	31.7	136	3.7
15	IV	A	95:5*	65*					139*	3.6*
CE 16	VI	none	100:0	32	3.9	3.08	0.18			
CE17	VII	none	100:0	8	3.7	4.31	0.13	30.5	136	2.8
18	VII	A	95:5*	15*						
CE19	VIII	none	100:0	116	5.6	4.79	0.37	56	116	3.3
CE 20	IX	none	100:0	123	4.5	3.40	0.25	68.7	121	3.8
21	VI	A	95:5***	41	4.8	3.90	0.26			
22	VI	A	90:10***	47	7.4	6.50	0.42			

10 \*blend prepared during film extrusion as outlined in Table 5

\*\*blend prepared by a single pelledsation on a twin screw APV 19TC25 extruder (screw diameter: 19 mm.  
L/D= 25) at an output rate of 1.2 kg/h

\*\*\* blend prepared by two successive pelletisations on a single screw Axon 18BX extruder (screw diameter: 18 mm/ L/D= 30) at an output rate of 1 kg/h

It can be seen from Table 6 that the higher melt strengths of the LDPE A used in the novel blends of the present invention would also lead to improvements in film processability, improved bubble stability as well as higher extrusion rates/temperatures as compared to LDPE B (e.g., Ex 4 exhibits higher melt strength at  $100 \text{ s}^{-1}$  shear rate,  $MS(100 \text{ s}^{-1})$ , than the Comparatives CE 6, CE 8, CE 14, CE 19 and CE 20).

10

**TABLE 7 - Film mechanical properties**

Example	Gloss (%)	Haze (%)	Dart Drop Impact (g)	Tear MD (g/25 $\mu\text{m}$ )	Tear TD (g/25 $\mu\text{m}$ )	MD Shrinkage (%)	Puncture resistance (N.cm/ $\mu\text{m}$ )
CE1	74	4.5	1550	179	449	7.6	7.0
2	75	4.3	1335	203	509	9.1	10.6
3	75	4.4	950	154	543	10.0	7.2
4	70	5.0	759	161	579	10.5	9.3
CE 5	51	9.4	407	124	594	16.1	9.6
CE 6	74	4.9	1705	201	412	6.1	7.6
CE 7	78	3.9	867	233	534	8.7	7.2
CE 8	79	3.4	777	160	585	9.6	6.4
CE 9*	34	20.4	1356	293	416	4.8	7.7
10	73	5.0	1083	220	463	5.6	6.9
CE 11	63	8.6	180	227	525	11.1***	5.8
12	75	5.5	159	156	539	13.9***	5.8
13	69	6.3	152	163	592	20.1***	5.7
CE 14	73	5.5	1665	181	452	6.5	6.9
15	72	5.2	1030	159	548	8.1	6.9
CE 16	79	3.2	2472	218	309	n/a	n/a
CE 17**	44	15	1540	276	346	n/a	n/a
18	77	4.2	1340	238	392	4.5	10.3
CE 19	60	7.9	800	125	469	14.6	9.2
CE 20	39	14.9	135	78	589	19.8***	5.7

\*: to achieve good bubble stability, frostline height had to be increased up to 650 mm (instead of 430 mm)

15 \*\*: extrusion was not possible under reference conditions. Extrusion temperature has been decreased down to 200°C (instead of 220°C)

\*\*\*: shrinkage measurements performed at 170°C (instead of 160°C).

**TABLE 8 - Film tensile properties**

Example	Secant Modulus (MPa)		Yield strength (MPa)		Tensile strength at break (MPa)		Elongation at break (%)	
	MD	TD	MD	TD	MD	TD	MD	TD
CE1	157	166	10.3	11.4	72	69	606	688
2	167	190	10.1	10.4	65	58	585	670
3	161	207	9.8	9.9	57	66	585	700
4	178	207	10.9	10.7	64	59	612	694
CE5	171	216	11.0	10.4	58	54	647	734
CE 6	154	198	9.9	10.1	63	64	569	671
CE 7	175	199	10.8	9.5	49	47	530	631
CE 8	180	204	11.5	10.6	65	57	636	683
CE 9*	154	157	10.7	10.9	68	67	631	693
10	175	185	10.2	11.5	64	55	669	665
CE 11	231	241	13.7	12.4	59	55	602	722
12	235	428	14.8	10.8	41	37	485	556
13	308	280	15.6	10.9	57	56	652	734
CE 14	179	176	10.0	14.2	60	52	495	607
15	170	232	10.0	15.5	68	40	548	525
CE 16	129	139	9.1	9.8	83	68	512	596
CE17**	152	154	9.3	13.9	69	63	576	625
18	164	186	10.5	9.3	73	60	625	638
CE 19	191	211	10.9	15	71	63	548	687
CE 20	262	278	14.1	11.4	59	43	549	655

5     \*: to achieve good bubble stability, frost-line height had to be increased up to 650 mm (instead of 430 mm)

     \*\*: extrusion was not possible under reference conditions. Extrusion temperature has been decreased down to 200°C (instead of 220°C).

10    It can be seen from Tables 7 and 8 that the use of the novel blends of the present invention would retain most of the film mechanical and tensile properties. For example, the Dart Drop Impact (DDI) strength of Ex 12 with 5% LDPE A blended to LLDPE III is about 90% that of the original (unblended) LLDPE III (i.e., Comparative CE 11). The selection of the LDPE A also leads to better residual DDI for the blends as compared to those with

15    LDPE B, namely Ex 3 with 5% LDPE A exhibits significantly higher DDI than those of Comparative CE 7 blend with 5% LDPE B in the same LLDPE I. That is, the former (Ex

3) blend retains greater 75% of the DDI of the original (or unblended) polymer as compared to about 50% DDI reduction of the latter (Comparative CE 7).

Claims:

1. A polymer blend comprising
  - (a) 90 - 97% by weight of a copolymer of ethylene and an alpha olefin having from 3 to
   
5 10 carbon atoms, said copolymer having
    - (i) a density in the range 0.910 to 0.940 g cm<sup>-3</sup>,
    - (ii) a melt index (190°C/2.16 kg), MI<sub>2</sub> < 5, and
    - (iii) molecular weight distribution ( $M_{w-cc}/M_{n-cc}$ , by classical GPC) in the range
   
2.0 - 5.0, and
  - 10 (b) from 3 - 10% by weight of a low density polyethylene polymer having
    - (i) a density from 0.910 to 0.920 g cm<sup>-3</sup>,
    - (ii) a melt index (190°C/2.16 kg), MI<sub>2</sub> > 2, and
    - (iii) a melt elastic modulus  $G'(G'' = 500 \text{ Pa}) \geq 140 \text{ Pa}$  at 190°C.

wherein the sum of (a) and (b) is 100%.
- 15 2. A polymer blend according to claim 1 wherein the copolymer of component (a) has a density in the range 0.912 to 0.935 g cm<sup>-3</sup> and preferably in the range 0.916 - 0.926 g cm<sup>3</sup>.
3. A polymer blend according to claim 1 wherein the copolymer of component (a) has a melt index (190°C/2.16 kg) in the range 0.1 to 4.0 and preferably in the range 0.5 to 3.0.
- 20 4. A polymer blend according to claim 1 wherein the copolymer of component (a) has a molecular weight distribution ( $M_{w-cc}/M_{n-cc}$ , by classical GPC) in the range 2.- to 4.2 and preferably in the range 3.0 to 4.0.
5. A polymer blend according to claim 1 wherein the copolymer of component (a) has a melt elastic modulus  $G'$  ( $G'' = 500\text{Pa}$ ) at 190°C in the range 25 to 70 Pa.
- 25 6. A polymer blend according to claim 1 wherein the copolymer of component (a) has a melt index ratio  $I_2)/I_2$  less than 35.
7. A polymer blend according to claim 1 wherein the copolymer of component (a) has a flow activation energy ( $E_a$ ) in the range 28 - 45 kJ/mol.
8. A polymer blend according to claim 1 wherein the copolymer of component (a) has
   
30 a Long Chain Branching Contraction Factor,  $g_{LCB} < 1$ .
9. A polymer blend according to claim 1 wherein the copolymer of component (a) has a melt strength pressure derivative at 190°C  $6(MS)/6P$  in the range 0.10 to 0.45 wherein



MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa.

10. A polymer blend according to claim 1 wherein the copolymer of component (a) has a melt strength shear rate derivative at 190°C  $6(MS)/5(\log \gamma)$  in the range 1.5 to 6.0
- 5 wherein MS is the melt strength of the copolymer in cN and  $\gamma$  is the capillary shear rate of the copolymer in  $s^{-1}$ .
11. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a density in the range 0.912 to 0.918  $g\ cm^{-3}$  and preferably in the range 0.914 to 0.918  $g\ cm^{-3}$ .
- 10 12. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a melt index (190°C/2.16 kg) in the range 3 to 8 and preferably in the range 3 to 6.
13. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a High Load Melt Index, HLMI (190°C/21.6 kg) in the range 80 - 160
- 15 and preferably in the range 130 - 160.
14. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a melt index ratio  $I_2/I_1$  at 190°C in the range 35 - 50.
15. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a molecular weight distribution ( $M_{w-cc}/M_{n-cc}$ , by classical GPC) in the
- 20 range 5 - 15.
16. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a flow activation energy ( $E_a$ ) at 190°C in the range 40 - 60 kJ/mol.
17. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a melt strength at shear rate of 100  $s^{-1}$ ,  $MS(100\ s^{-1})$  at 190°C of  $\geq 10$  cN
- 25 and most preferably in the range 12 - 20 cN.
18. A polymer blend according to claim 1 wherein the low density polyethylene of component (b) has a weight-average molecular weight ratio,  $M_{wL}/M_{w-cc,lib} > 2.5$  and more preferably greater than 3.
19. A polymer blend according to any of the preceding claims comprising 92 to 97%
- 30 by weight of component (a) and 3 to 8 % by weight of component (b).
20. A polymer blend according to claim 19 comprising 93 to 96% by weight of component (a) and 4 to 7 % by weight of component (b).

21. A polymer blend according to claim 19 wherein component (a) has a melt strength pressure derivative at 190°C 6(MS)/8P in the range 0.10 to 0.45 and component (b) has a melt strength at shear rate of 100 s<sup>-1</sup>, MS(100 s<sup>-1</sup>) at 190°C of  $\geq 10$  cN
22. A polymer blend according to claim 19 wherein component (a) has a Long Chain  
5 Branching Contraction Factor,  $g_{LCB} < 1$  and component (b) has a weight-average molecular weight ratio,  $M_{wLS}/M_{w-c_{lib}} > 2.5$ .
23. A polymer blend according to claim 19 wherein component (a) has a melt index ratio I21/I2 less than 35 and component (b) has a High Load Melt Index, HLMI (190°C/21.6 kg) in the range 80 - 160.
- 10 24. A polymer blend according to claim 19 wherein component (a) has a molecular weight distribution ( $M_{w-c}/M_{n-c}$ , by classical GPC) in the range 2.- to 4.2 and component (b) has a molecular weight distribution ( $M_{w-c}/M_{n-c}$ , by classical GPC) in the range 5 - 15.
25. A polymer blend according to any of the preceding claims wherein the copolymer of component (a) is prepared by use of a metallocene catalyst system.
- 15 26. A polymer blend according to claim 19, wherein the copolymer of component (a) has a density in the range 0.916 to 0.926 g cm<sup>-3</sup>, said blend exhibiting an Energy Index (EI) that is at least 5%, preferably in the range 5 - 11% and more preferably in the range 6 - 10%, lower than the Energy Index (EI) exhibited by the copolymer of component (a) of the blend alone during blown film extrusion.
- 20 27. A polymer blend according to claim 19 having:
- (i) a melt elasticity at 190°C,  $G'(G''=500 \text{ Pa}) \leq 110 \text{ Pa}$ , preferably in the range 40 - 80 Pa and more preferably in the range 40 - 70 Pa,
  - (ii) a melt strength at 100 s<sup>-1</sup> shear rate at 190°C,  $MS(100 \text{ s}^{-1}) \geq 5.6 \text{ cN}$ , preferably in the range 5.7 - 9.0 cN and more preferably in the range 5.7 - 8.0 cN, and
  - 25 (iii) a melt Strength shear rate derivative at 190°C,  $5(MS)/5(\log \dot{\gamma}) \geq 5 \text{ cN}$ , preferably in the range 5.0 - 7.0 cN.
28. A film comprising the polymer blend according to any of claims 1 - 27.
29. A blown film (25  $\mu\text{m}$ ) comprising a polymer blend according to claim 28 having a  
30 drop Dart Impact strength [ISO 7765-1 (1988) (Method A) of at least 50%, preferably in the range 60 - 95% and more preferably in the range 70 - 90% more than a film comprising the copolymer of component (a) of the blend alone.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/074076

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C08L23/08 C08J5/18  
ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C08L C08J C09D

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

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

EPO-Internal , WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/074076

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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