(54) Titre : COMPOSITION DE POLYETHYLENE PRESENTANT UNE RESISTANCE A LA FISSURATION SOUS
CONTRAINTE DANS UN ENVIRONNEMENT DONNE
(54) Title: POLYETHYLENE COMPOSITION HAVING ENVIRONMENTAL STRESS CRACKING RESISTANCE
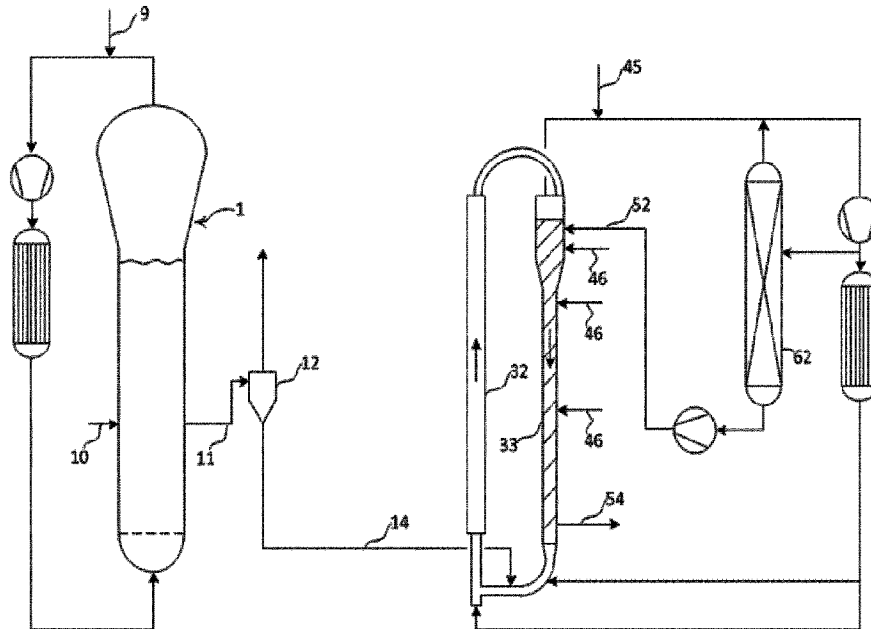
(57) Abrégé/Abstract:

The present disclosure relates to a polyethylene composition particularly suited for producing blow-molded hollow articles, having the following features: 1) density from 0.940 to 0.955 g/cm^3, determined according to ISO 1183 at 23°C; 2) ratio MIF/MIP from 12 to 40; 3) Mz from 500,000 to 3,500,000 g/mol; 4) ?0.02 from 80,000 to 300,000 Pa.s; 5) HMWcopo index from 1 to 15; and 6) Mz/Mw*LCBI lower than 6.4.

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(54) **Title:** POLYETHYLENE COMPOSITION HAVING ENVIRONMENTAL STRESS CRACKING RESISTANCE

Fig. 1

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POLYETHYLENE COMPOSITION HAVING ENVIRONMENTAL STRESS CRACKING RESISTANCE

FIELD OF THE INVENTION

[0001]   The present disclosure relates to a polyethylene composition suitable for preparing various kinds of formed articles. In particular, due to its enhanced environmental stress cracking resistance (FNCT) and impact resistance, high-quality surface and dimension stability of final article, the present composition is suitable for making extrusion blow-molded hollow articles, such as drums, containers and gasoline storage tanks.

BACKGROUND OF THE INVENTION

[0002]   The present polyethylene composition provides an unmatched balance of mechanical properties and process-ability with respect to the known polyethylene compositions for the same use, as disclosed in particular in US6201078 and WO2014064062.

SUMMARY OF THE INVENTION

[0003]   The present disclosure provides a polyethylene composition having the following features:

1)   density from 0.940 to 0.955 g/cm^3, preferably from 0.940 to 0.951 g/cm^3, in particular from 0.945 to 0.952 g/cm^3, or from 0.946 to 0.952 g/cm^3, or from 0.945 to 0.951 g/cm^3, or from 0.946 to 0.951 g/cm^3, determined according to ISO 1183 at 23°C;

2)   ratio MIF/MIP from 12 to 40, in particular from 15 to 38 or from 17 to 35, where MIF is the melt flow index at 190°C with a load of 21.60 kg, and MIP is the melt flow index at 190°C with a load of 5 kg, both determined according to ISO 1133-1;

3)   Mz from 500,000 to 3,500,000 g/mol, preferably from 800,000 to 3,300,000 g/mol, in particular from 800,000 to 3,000,000 g/mol, where Mz is the z-average molecular weight, measured by GPC;

4) $\eta_{0.02}$ from 80,000 to 300,000 Pa.s, or from 85,000 to 250,000 Pa.s, wherein $\eta_{0.02}$ is the complex shear viscosity at an angular frequency of 0.02 rad/s, measured with dynamic oscillatory shear in a plate-plate rotational rheometer at a temperature of 190°C;

5)   HMWcopo index from 1 to 15, preferably from 1 to 14, in particular from 1 to 10 or from 1 to 9 or from 1 to 8;

wherein the HMWcopo index is determined according to the following formula:

$$\text{HMWcopo} = (\eta_{0.02} \times t_{maxDSC})/(10^{\wedge}5)$$

where $\eta_{0.02}$ is the complex shear viscosity of the melt in Pa.s, measured at a temperature of 190°C, in a parallel-plate (or so-called plate-plate) rheometer under dynamic oscillatory shear mode with an applied angular frequency of 0.02 rad/s; the t_{maxDSC} is the time, in minutes, required to reach the maximum value of heat flow (in mW) of crystallization (time at which the maximum crystallization rate is achieved, equivalent to the $t_{1/2}$ crystallization half-time) at a temperature of 124 °C under quiescent conditions, measured in isothermal mode in a differential scanning calorimetry apparatus, DSC;

6)   Mz/Mw*LCBI of lower than 6.4;

wherein LCBI (Long-Chain Branching Index) is the ratio of the measured mean-square radius of gyration Rg, measured by GPC-MALLS, to the mean-square radius of gyration for a linear PE having the same molecular weight at a mol. weight of 1,000,000 g/mol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004]   These and other features, aspects, and advantages of the present disclosure will become better understood with reference to the following description and appended claims, and accompanying drawing figure where:

The drawing is an illustrative embodiment of a simplified process-flow diagram of two serially connected gas-phase reactors suitable for use in accordance with various embodiments of ethylene polymerization processes disclosed herein to produce various embodiments of the polyethylene compositions disclosed herein.

[0005]   It should be understood that the various embodiments are not limited to the arrangements and instrumentality shown in the drawing figure.

DETAILED DESCRIPTION OF THE INVENTION

[0006]   The expression "polyethylene composition" is intended to embrace, as alternatives, both a single ethylene polymer and an ethylene polymer composition, in particular a composition of two or more ethylene polymer components, preferably with different molecular weights, such composition being also called "bimodal" or "multimodal" polymer in the relevant art.

[0007]   Typically the present polyethylene composition consists of or comprises one or more ethylene copolymers.

[0008]   All the features herein defined, comprising the previously defined features 1) to 6), are referred to the said ethylene polymer or ethylene polymer composition. The addition of

other components, like the additives normally employed in the art, can modify one or more of said features.

[0009]   The ratio MIF/MIP provides a rheological measure of molecular weight distribution.

[0010]   Another measure of the molecular weight distribution is provided by the ratio M_w /M_n, where M_w is the weight average molecular weight and M_n is the number average molecular weight, measured by GPC (Gel Permeation Chromatography), as explained in the examples.

[0011]   Preferred M_w /M_n values for the present polyethylene composition range from 15 to 40, in particular from 20 to 35.

[0012]   The M_w values are preferably from 150,000 g/mol to 500,000 g/mol, in particular from 200,000 g/mol to 450,000 g/mol.

[0013]   Preferred values of Mz/Mw*LCBI, which is Mz/Mw multiplied by LCBI, are equal to or lower than 6.0, in particular equal to or lower than 5.9.

[0014]   Preferred ranges of Mz/Mw*LCBI are:

[0015]   - from 3.2 to lower than 6.4; or

[0016]   - from 3.2 to 6.0; or

[0017]   - from 3.2 to 5.9; or

[0018]   - from 3.5 to lower than 6.4; or

[0019]   - from 3.5 to 6.0; or

[0020]   - from 3.5 to 5.9.

[0021]   Moreover the present polyethylene composition has preferably at least one of the following additional features.

- MIF from 4 to 15 g/10min., in particular from 5 to 12 g/10min.;

- ratio ($\eta_{0.02}$ /1000)/ LCBI, which is between $\eta_{0.02}$ divided by 1000 and LCBI, equal to or greater than 150, or greater than 190, in particular from 150 to 300, or from 190 to 300, or from 190 to 250;

- comonomer content equal to or less than 2% by weight, in particular from 0.5 to 2% by weight, with respect to the total weight of the composition;

- LCBI equal to or greater than 0.65, preferably equal to or greater than 0.70, in particular equal to or greater than 0.72,

[0022]   Preferred ranges of LCBI values are:

[0023]   - from 0.65 to 0.90; or

[0024]   - from 0.65 to 0.85; or

[0025]   - from 0.70 to 0.90; or

[0026]   - from 0.70 to 0.85; or

[0027]   - from 0.70 to 0.82; or

[0028]   - from 0.72 to 0.90; or

[0029]   - from 0.72 to 0.85; or

[0030]   - from 0.72 to 0.82.

[0031]   The comonomer or comonomers present in the ethylene copolymers are generally selected from olefins having the general formula $CH_2=CHR$ wherein R is an alkyl radical, linear or branched, having from 1 to 10 carbon atoms.

[0032]   Specific examples are propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1 and decene-1. A particularly preferred comonomer is hexene-1.

[0033]   In particular, in a preferred embodiment, the present composition comprises:

A)   30 – 70% by weight, preferably 40 – 60% by weight of an ethylene homopolymer or copolymer (the homopolymer being preferred) with density equal to or greater than 0.960 g/cm^3 and melt flow index MIE at 190°C with a load of 2.16 kg, according to ISO 1133, of 2 g/10 min. or higher, preferably of 5 g/10 min. or higher;

B)   30 – 70% by weight, preferably 40 – 60% by weight of an ethylene copolymer having a MIE value lower than the MIE value of A), preferably lower than 0.5 g/10 min.

[0034]   The above percent amounts are given with respect to the total weight of A) + B).

[0035]   Specific MIE ranges for component A) are:

[0036]   - 2 to 20 g/10 min.; or

[0037]   - 3 to 20 g/10 min.; or

[0038]   - 2 to 15 g/10 min.; or

[0039]   - 3 to 15 g/10 min.

[0040]   As previously said, the present polyethylene composition can be advantageously used for producing blow molded articles.

[0041]   In fact it is preferably characterized by the following properties:

- Environmental stress crack resistance measured by FNCT 4 MPa/80°C higher than 500h, in particular higher than 800h;

- Swell ratio higher than 140%;

- Notched Tensile Impact AZK at -30°C of 80 kJ/m^2 or higher;

- Substantial absence of gels having gel diameter of higher than 700 µm.

[0042]   The details of the test methods are given in the examples.

[0043]   The blow-molding process is generally carried out by first plastifying the polyethylene composition in an extruder at temperatures in the range from 180 to 250°C and then extruding it through a die into a blow mold, where it is cooled.

[0044] While no necessary limitation is known to exist in principle on the kind of polymerization processes and catalysts to be used, it has been found that the present polyethylene composition can be prepared by a gas phase polymerization process in the presence of a Ziegler-Natta catalyst.

[0045] A Ziegler-Natta catalyst comprises the product of the reaction of an organometallic compound of group 1, 2 or 13 of the Periodic Table of elements with a transition metal compound of groups 4 to 10 of the Periodic Table of Elements (new notation). In particular, the transition metal compound can be selected among compounds of Ti, V, Zr, Cr and Hf and is preferably supported on $MgCl_2$.

[0046] Preferred organometallic compounds are the organo-Al compounds.

[0047] Thus in a preferred embodiment, the present polyethylene composition is obtainable by using a Ziegler-Natta polymerization catalyst, preferably a Ziegler-Natta catalyst comprising the product of reaction of:

A)   a solid catalyst component comprising a Ti, Mg, chlorine and one or more internal electron donor compounds ED;

B)   an organo-Al compound; and optionally

C)   an external electron donor compound ED_{ext}.

[0048] In particular, the solid catalyst component A) comprises one internal electron donor ED selected from esters of aliphatic monocarboxylic acids (EAA) and another internal donor ED^I selected from cyclic ethers (CE) in an amount such that the EAA/CE molar ratio ranges from 0.02 to less than 20.

[0049] Preferably, the EAA/CE molar ratio ranges from 0.2 to 16 and more preferably from 0.5 to 10.

[0050] The internal electron donor compound (EAA) is preferably selected from C_1-C_{10}, preferably C_2-C_5 alkyl esters of C_2-C_{10}, preferably C_2-C_6, aliphatic monocarboxylic acids. Among them, particularly preferred is ethyl acetate.

[0051] The (CE) internal donor is preferably selected from cyclic ethers having 3-5 carbon atoms and, among them, tetrahydrofuran, tetrahydropirane and dioxane are the most preferred with tetrahydrofuran being especially preferred.

[0052] The (EAA+CE)/Ti molar ratio is preferably higher than 1.5, and more preferably ranges from 2.0 to 10, especially from 2.5 to 8.

[0053] The content of (EAA) typically ranges from 1 to 30%wt with respect to the total weight of the solid catalyst component, more preferably from 2 to 20%wt. The content of (CE) typically ranges from 1 to 20%wt with respect to the total weight of the solid catalyst component, more preferably from 2 to 10%wt.

[0054] The Mg/Ti molar ratio preferably ranges from 5 to 50, more preferably from 10 to 40.

[0055] As disclosed above the catalyst component comprises, in addition to the electron donor compounds, Ti, Mg and chlorine. The Ti atoms preferably derive from a Ti compound containing at least a Ti-halogen bond and the Mg atoms preferably derive from a magnesium dichloride. Preferred titanium compounds are the tetrahalides or the compounds of formula $TiX_n(OR^1)_{4-n}$, where $0<n<3$, X is halogen, preferably chlorine, and R^1 is C_1-C_{10} hydrocarbon group. Titanium tetrachloride is the preferred titanium compound.

[0056] The catalyst component of the present disclosure can be prepared according to different methods.

[0057] One preferred method comprises the following steps: (a) contacting a $MgX_2(R^2OH)_m$ adduct in which R^2 groups are C_1-C_{20} hydrocarbon groups and X is halogen, with a liquid medium comprising a Ti compound having at least a Ti-Cl bond, in an amount such that the Ti/Mg molar ratio is greater than 3, thereby forming a solid intermediate;

[0058] (b) contacting the internal donor compounds (EAA) and (CE) as previously defined with the solid intermediate product coming from (a) followed by washing the resulting product.

[0059] Preferred starting $MgX_2(R^2OH)_m$ adducts are those in which R^2 groups are C_1-C_{10} alkyl groups, X is chlorine and m is from 0.5 to 4, more preferably from 0.5 to 2. Adducts of this type can generally be obtained by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Representative methods for the preparation of these spherical adducts are reported for example in USP 4,469,648, USP 4,399,054, and WO98/44009. Another useable method for the spherulization is the spray cooling method described for example in USP 5,100,849 and 4,829,034.

[0060] Particularly interesting are the $MgCl_2(EtOH)_m$ adducts in which m is from 0.15 to 1.5 and particle size ranging from 10 to 100 μm obtained by subjecting the adducts with a higher alcohol content to a thermal dealcoholation process carried out in nitrogen flow at temperatures comprised between 50 and 150°C until the alcohol content is reduced to the above value. A process of this type is described in EP 395083.

[0061] The dealcoholation can also be carried out chemically by contacting the adduct with compounds capable of reacting with the alcohol groups.

[0062]   Generally these dealcoholated adducts are also characterized by a porosity (measured by mercury method) due to pores with radius up to 1μm ranging from 0.15 to 2.5 cm^3/g, preferably from 0.25 to 1.5 cm^3/g.

[0063]   The reaction with the Ti compound can be carried out by suspending the adduct in $TiCl_4$ (which is generally cold); subsequently the mixture is heated up to temperatures ranging from 80-130°C and kept at this temperature for 0.5-2 hours. The treatment with the titanium compound can be carried out one or more times. Preferably, it is carried out two times. At the end of the process the intermediate solid is recovered by separation of the suspension via the conventional methods (such as settling and removing of the liquid, filtration and centrifugation) and can be subject to washings with solvents. Although the washings are typically carried out with inert hydrocarbon liquids, it is also possible to use more polar solvents (having for example a higher dielectric constant) such as halogenated hydrocarbons.

[0064]   As mentioned above, the intermediate solid is, in step (b) brought into contact with the internal donor compounds under conditions such as to fix on the solid an amount of donors such that the EAA/CE molar ratio ranging from 0.02 to less than 20 is fulfilled.

[0065]   Although not strictly required the contact is typically carried out in a liquid medium such as a liquid hydrocarbon. The temperature at which the contact takes place can vary depending on the nature of the reagents. Generally, it is comprised in the range from -10° to 150°C and preferably from 0° to 120°C. It is clear that temperatures causing the decomposition or degradation of any specific reagents should be avoided even if they fall within the generally suitable range. Also the time of the treatment can vary in dependence of other conditions such as the nature of the reagents, temperature, concentration etc. As a general indication, this contact step can last from 10 minutes to 10 hours more frequently from 0.5 to 5 hours. If desired, in order to further increase the final donor content, this step can be repeated one or more times.

[0066]   At the end of this step the solid is recovered by separation of the suspension via conventional methods (such as settling and removing of the liquid, filtration and centrifugation) and can be subject to washings with solvents. Although the washings are typically carried out with inert hydrocarbon liquids, it is also possible to use more polar solvents (having, for example, a higher dielectric constant) such as halogenated or oxygenated hydrocarbons.

[0067]   According to a specific embodiment, it is particularly preferred that after step (b) a further step (c) is carried out by subjecting the solid catalyst component coming from (b) to a thermal treatment carried out at a temperature from 70 to 150°C.

[0068]   In step (c) of the method, the solid product recovered from step (b) is subject to a thermal treatment carried out at temperatures ranging from 70 to 150°C, preferably from 80°C to 130°C, and more preferably from 85 to 100°C.

[0069]   The thermal treatment can be carried out in several ways. According to one of them the solid coming from step (b) is suspended in an inert diluent like a hydrocarbon and then subject to the heating while maintaining the system under stirring.

[0070]   According to an alternative technique, the solid can be heated in a dry state by inserting it in a device having jacketed heated walls. While stirring can be provided by means of mechanical stirrers placed within said device, it is preferred to cause stirring to take place by using rotating devices.

[0071]   According to a still different embodiment the solid coming from (b) can be heated by subjecting it to a flow of hot inert gas such as nitrogen, preferably by maintaining the solid under fluidization conditions.

[0072]   The heating time is not fixed but may vary depending on other conditions such as the maximum temperature reached. It generally ranges from 0.1 to 10 hours, more specifically from 0.5 to 6 hours. Usually, higher temperatures allow the heating time to be shorter while lower temperatures may require longer reaction times.

[0073]   In the process as described, each of the steps (b)-(c) can be carried out immediately after the previous step, without the need of isolating the solid product coming from that previous step. However, if desired the solid product coming from one step can be isolated and washed before being subject to the subsequent step.

[0074]   According to a specific embodiment, a preferred modification of the process comprises subjecting the solid coming from step (a) to a prepolymerization step (a2) before carrying out step (b).

[0075]   The pre-polymerization can be carried out with any of the olefins $CH_2=CHR$, where R is H or a C_1-C_{10} hydrocarbon group. In particular, it is especially preferred to pre-polymerize ethylene or propylene or mixtures thereof with one or more α-olefins, said mixtures containing up to 20% in moles of α-olefin, forming amounts of polymer from about 0.1 g up to about 1000 g per gram of solid intermediate, preferably from about 0.5 to about 500 g per gram of solid intermediate, more preferably from 0.5 to 50 g per gram of solid intermediate and especially from 0.5 to 5 g per gram of solid intermediate. The pre-polymerization step can be carried out at temperatures from 0 to 80°C, preferably from 5 to 70°C, in the liquid or gas phase. The pre-polymerization of the intermediate with ethylene or propylene in order to produce an amount of polymer ranging from 0.5 to 20 g per gram of intermediate is particularly preferred. The pre-polymerization is carried out with the use of a

suitable cocatalyst such as organoaluminum compounds. When the solid intermediate is prepolymerized with propylene it is especially preferred that the prepolymerization is carried out in the presence of one or more external donors preferably selected from the group consisting of silicon compounds of the general formula $R_a^4R_b^5Si(OR^6)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^4, R^5, and R^6, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^4 and R^5 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms, and R^6 is a C_1-C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane (C donor), diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane (D donor) and diisopropyldimethoxysilane

[0076] All of the above mentioned processes are suitable for the preparation of particles of solid catalyst components having substantially spherical morphology and average diameter comprised between 5 and 150 μm, preferably from 10 to 100 μm. As particles having substantially spherical morphology, those are meant wherein the ratio between the greater axis and the smaller axis is equal to, or lower than 1.5, and preferably lower than 1.3.

[0077] Generally, the solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 10 and 200 m²/g and preferably between 20 and 80 m²/g, and a total porosity (by B.E.T. method) higher than 0.15 cm³/g preferably between 0.2 and 0.6 cm³/g. The porosity (Hg method) due to pores with radius up to 10.000 Å generally ranges from 0.25 to 1 cm³/g, preferably from 0.35 to 0.8 cm³/g.

[0078] As previously explained, the catalyst components of the disclosure form polymerization catalysts by reaction with Al-alkyl compounds. In particular Al-trialkyl compounds, for example Al-trimethyl, Al-triethyl, Al-tri-n-butyl, Al-triisobutyl are preferred. The Al/Ti ratio is higher than 1 and is generally comprised between 5 and 800.

[0079] Also, alkylaluminum halides and in particular alkylaluminum chlorides such as diethylaluminum chloride (DEAC), diisobutylaluminum chloride, Al-sesquichloride and dimethylaluminum chloride (DMAC) can be used. It is also possible to use, and in certain cases preferred, mixtures of trialkylaluminum compounds with alkylaluminum halides. Among them mixtures TEAL/DEAC and TIBA/DEAC are particularly preferred.

[0080] Optionally, an external electron donor (ED_ext) can be used during polymerization. The external electron donor compound can be equal to, or different from, the internal donors used in the solid catalyst component. Preferably, it is selected from the group consisting of ethers, esters, amines, ketones, nitriles, silanes and mixtures of the above. In particular, it can

advantageously be selected from the C_2-C_{20} aliphatic ethers and especially from cyclic ethers preferably having 3-5 carbon atoms such as tetrahydrofuran and dioxane.

[0081] In addition to the aluminium alkyl cocatalyst (B) and the possible use of an external electron donor (ED_{ext}) as a component (C), it is possible to use a halogenated compound (D) as activity enhancer. Said compound is preferably a mono- or dihalogenated hydrocarbon. In one preferred embodiment, it is chosen among monohalogenated hydrocarbons in which the halogen is linked to a secondary carbon atom. The halogen is preferably chosen from among chloride and bromide.

[0082] Non-limiting exemplary compounds for (D) are propylchloride, i-propylchloride, butylchloride, s-butylchloride, t-butylchloride 2-chlorobutane, cyclopentylchloride, cyclohexylchloride, 1,2-dichloroethane, 1,6-dichlorohexane, propylbromide, i-propylbromide, butylbromide, s-butylbromide, t-butylbromide, i-butylbromide i-pentylbromide, and t-pentylbromide. Among them, particularly preferred are i-propylchloride, 2-chlorobutane, cyclopentylchloride, cyclohexylchloride, 1,4-dichlorobutane and 2-bromopropane.

[0083] According to another embodiment the compounds can be chosen from among halogenated alcohols, esters or ethers such as 2,2,2,-trichloroethanol, ethyl trichloroacetate, butyl perchlorocrotonate, 2-chloro propionate and 2-chloro-tetrahydrofurane.

[0084] The activity enhancer can be used in amounts such as to have the (B)/(D) molar ratio of higher than 3 and preferably in the range 5-50 and more preferably in the range 10-40.

[0085] The above mentioned components (A)-(D) can be fed separately into the reactor under the polymerization conditions to exploit their activity. It constitutes however a particular advantageous embodiment the pre-contact of the above components, optionally in the presence of small amounts of olefins, over a period of time ranging from 1 minute to 10 hours, preferably in the range from 2 to 7 hours. The pre-contact can be carried out in a liquid diluent at a temperature ranging from 0 to 90°C preferably in the range of 20 to 70°C.

[0086] One or more alkyl aluminum compound or mixtures thereof can be used in the pre-contact. If more than one alkylaluminum compound is used in the pre-contact, they can be used altogether or added sequentially to the pre-contact tank. Even if the pre-contact is carried out, it is not necessary to add at this stage the whole amount of aluminum alkyl compounds. A portion thereof can be added in the pre-contact while the remaining aliquot can be fed to the polymerization reactor. Moreover, when more than one aluminum alkyl compound is used, it is also possible using one or more in the precontact process and the other(s) fed to the reactor.

[0087] In one of the preferred embodiments, a precontact is carried out by first contacting the catalyst component with an aluminum trialkyl such as tri-n-hexyl aluminum (THA), then

another aluminum alkyl compound, preferably, diethylaluminum chloride is added to the mixture, and finally as a third component another trialkylaluminum, preferably, triethylaluminum is added to the pre-contact mixture. According to a variant of this method, the last aluminum trialkyl is added to the polymerization reactor.

[0088]   The total amount of aluminum alkyl compounds used can vary within broad ranges, but it preferably ranges from 2 to 10 mols per mole of internal donor in the solid catalyst component.

[0089]   It has been found that by using the above described polymerization catalyst, the polyethylene composition of the present invention can be prepared in a process comprising the following steps, in any mutual order:

a)   polymerizing ethylene, optionally together with one or more comonomers, in a gas-phase reactor in the presence of hydrogen;

b)   copolymerizing ethylene with one or more comonomers in another gas-phase reactor in the presence of an amount of hydrogen less than step a);

where in at least one of said gas-phase reactors the growing polymer particles flow upward through a first polymerization zone (riser) under fast fluidization or transport conditions, leave said riser and enter a second polymerization zone (downcomer) through which they flow downward under the action of gravity, leave said downcomer and are reintroduced into the riser, thus establishing a circulation of polymer between said two polymerization zones.

[0090]   In the first polymerization zone (riser), fast fluidization conditions are established by feeding a gas mixture comprising one or more olefins (ethylene and comonomers) at a velocity higher than the transport velocity of the polymer particles. The velocity of said gas mixture is preferably comprised between 0.5 and 15 m/s, more preferably between 0.8 and 5 m/s. The terms "transport velocity" and "fast fluidization conditions" are well known in the art; for a definition thereof, see, for example, "D. Geldart, Gas Fluidisation Technology, page 155 et seq. , J. Wiley & Sons Ltd. , 1986".

[0091]   In the second polymerization zone (downcomer), the polymer particles flow under the action of gravity in a densified form, so that high values of density of the solid are reached (mass of polymer per volume of reactor), which approach the bulk density of the polymer.

[0092]   In other words, the polymer flows vertically down through the downcomer in a plug flow (packed flow mode), so that only small quantities of gas are entrained between the polymer particles.

[0093]   Such process allows to obtain from step a) an ethylene polymer with a molecular weight lower than the ethylene copolymer obtained from step b).

[0094]   Preferably, a polymerization of ethylene to produce a relatively low molecular weight ethylene copolymer (step a) is performed upstream the copolymerization of ethylene to produce a relatively high molecular weight ethylene copolymer (step b). To this aim, in step a) a gaseous mixture comprising ethylene, hydrogen, optionally comonomer and an inert gas is fed to a first gas-phase reactor, preferably a gas-phase fluidized bed reactor. The polymerization is carried out in the presence of the previously described Ziegler-Natta catalyst.

[0095]   Hydrogen is fed in an amount depending on the specific catalyst used and, in any case, suitable to obtain in step a) an ethylene polymer with a melt flow index MIE of 5 g/10 min. or higher. In order to obtain the above MIE range, in step a) the hydrogen/ethylene molar ratio is indicatively from 0.8 to 3, the amount of ethylene monomer being from 2 to 20% by volume, preferably from 5 to15% by volume, based on the total volume of gas present in the polymerization reactor. The remaining portion of the feeding mixture is represented by inert gases and one or more comonomers, if any. Inert gases which are necessary to dissipate the heat generated by the polymerization reaction are conveniently selected from nitrogen or saturated hydrocarbons, the most preferred being propane.

[0096]   The operating temperature in the reactor of step a) is selected between 50 and 120°C, preferably between 65 and 100°C, while the operating pressure is between 0.5 and 10 MPa, preferably between 2.0 and 3.5 MPa.

[0097]   In a preferred embodiment, the ethylene polymer obtained in step a) represents from 30 to 70% by weight of the total ethylene polymer produced in the overall process, i. e. in the first and second serially connected reactors.

[0098]   The ethylene polymer coming from step a) and the entrained gas are then passed through a solid/gas separation step, in order to prevent the gaseous mixture coming from the first polymerization reactor from entering the reactor of step b) (second gas-phase polymerization reactor). Said gaseous mixture can be recycled back to the first polymerization reactor, while the separated ethylene polymer is fed to the reactor of step b). A suitable point of feeding of the polymer into the second reactor is on the connecting part between the downcomer and the riser, wherein the solid concentration is particularly low, so that the flow conditions are not negatively affected.

[0099]   The operating temperature in step b) is in the range of 65 to 95°C, and the pressure is in the range of 1.5 to 4.0 MPa. The second gas-phase reactor is aimed to produce a relatively high molecular weight ethylene copolymer by copolymerizing ethylene with one or more comonomers. Furthermore, in order to broaden the molecular weight distribution of the final ethylene polymer, the reactor of step b) can be conveniently operated by establishing different conditions of monomers and hydrogen concentration within the riser and the downcomer.

[0100]   To this purpose, in step b) the gas mixture entraining the polymer particles and coming from the riser can be partially or totally prevented from entering the downcomer, so as to obtain two different gas composition zones. This can be achieved by feeding a gas and/or a liquid mixture into the downcomer through a line placed at a suitable point of the downcomer, preferably in the upper part thereof. Said gas and/or liquid mixture should have a suitable composition, different from that of the gas mixture present in the riser. The flow of said gas and/or liquid mixture can be regulated so that an upward flow of gas counter-current to the flow of the polymer particles is generated, particularly at the top thereof, acting as a barrier to the gas mixture entrained among the polymer particles coming from the riser. In particular, it is advantageous to feed a mixture with low content of hydrogen in order to produce the higher molecular weight polymer fraction in the downcomer. One or more comonomers can be fed to the downcomer of step b), optionally together with ethylene, propane or other inert gases.

[0101]   The hydrogen/ethylene molar ratio in the downcomer of step b) is comprised between 0.005 and 0.2, the ethylene concentration being comprised from 0.5 to 15%, preferably 0.5 - 10%, by volume, the comonomer concentration being comprised from 0.1 to 1.5 % by volume, based on the total volume of gas present in said downcomer. The rest is propane or similar inert gases. Since a very low molar concentration of hydrogen is present in the downcomer, by carrying out the present process it is possible to bond a relatively high amount of comonomer to the high molecular weight polyethylene fraction.

[0102]   The polymer particles coming from the downcomer are reintroduced in the riser of step b).

[0103]   Since the polymer particles keep reacting and no more comonomer is fed to the riser, the concentration of said comonomer drops to a range of 0.1 to 1.2 % by volume, based on the total volume of gas present in said riser. In practice, the comonomer content is controlled in order to obtain the desired density of the final polyethylene. In the riser of step b) the hydrogen/ethylene molar ratio is in the range of 0.01 to 0.5, the ethylene concentration being comprised between 5 and 20 % by volume based on the total volume of gas present in said riser. The rest is propane or other inert gases.

[0104]   More details on the above described polymerization process are provided in WO2005019280.

EXAMPLES

[0105]   The practice and advantages of the various embodiments, compositions and methods as provided herein are disclosed below in the following examples. These Examples

are illustrative only, and are not intended to limit the scope of the appended claims in any manner whatsoever.

[0106] The following analytical methods are used to characterize the polymer compositions.

[0107] <u>Density</u>

[0108] Determined according to ISO 1183 at 23°C.

[0109] <u>Complex shear viscosity $\eta_{0.02}$ (eta (0.02))</u>

Measured at angular frequency of 0.02 rad/s and 190°C as follows.

Samples are melt-pressed for 4 min under 200 °C and 200 bar into plates of 1mm thickness. Disc specimens of a diameter of 25 mm are stamped and inserted in the rheometer, which is pre-heated at 190 °C. The measurement can be performed using any rotational rheometer commercially available. Here the Anton Paar MCR 300 is utilized, with a plate-plate geometry. A so-called frequency-sweep is performed (after 4 min of annealing the sample at the measurement temperature) at T = 190 °C, under constant strain-amplitude of 5%, measuring and analyzing the stress response of the material in the range of excitation frequencies ω from 628 to 0.02 rad/s. The standardized basic software is utilized to calculate the rheological properties, i.e. the storage-modulus, G', the loss-modulus, G'', the phase lag δ (=arctan(G''/G')) and the complex viscosity, η^*, as a function of the applied frequency, namely $\eta^*(\omega) = [G'(\omega)^2 + G''(\omega)^2]^{1/2}/\omega$. The value of the latter at an applied frequency ω of 0.02 rad/s is the $\eta_{0.02}$.

[0110] <u>HMWcopo Index</u>

[0111] In order to quantify the crystallization and processability potential of the polymer, the HMWcopo (High Molecular Weight Copolymer) Index is used, which is defined by the following formula:

$$HMWcopo = (\eta_{0.02} \times t_{maxDSC})/(10^5)$$

[0112] It is decreasing with increasing potential of easy processing (low melt-viscosity) and fast crystallization of the polymer. It is also a description and quantification of the amount of high molecular weight fraction, correlating to the melt complex shear viscosity $\eta_{0.02}$ at the frequency of 0.02 rad/s, measured as above described, and the amount of incorporated comonomer which delays the crystallization, as quantified by the maximum heat flow time for quiescent crystallization, t_{maxDSC}.

[0113] The t_{maxDSC} is determined using a Differential Scanning Calorimetry apparatus, TA Instruments Q2000, under isothermal conditions at a constant temperature of 124 °C. 5-6 mg of sample are weighted and brought into the aluminium DSC pans. The sample is heated at a rate of 20K/min up to 200 °C and cooled down also with 20K/min to the test temperature, in

order to erase the thermal history. The isothermal test begins immediately afterwards and the time is recorded until crystallization occurs. The time interval until the crystallization heat flow maximum (peak), t_{maxDSC}, is determined using the vendor software (TA Instruments). The measurement is repeated 3x times and an average value is then calculated (in min). If no crystallization is observed under these conditions for more than 120 minutes, the value of t_{maxDSC} = 120 minutes is used for further calculations of the HMWcopo index.

[0114]   The melt viscosity $\eta_{0.02}$ value is multiplied by the t_{maxDSC} value and the product is normalized by a factor of 100000 (10^5).

[0115]   **Molecular Weight Distribution Determination**

[0116]   The determination of the molar mass distributions and the means Mn, Mw, Mz and Mw/Mn derived therefrom was carried out by high-temperature gel permeation chromatography using a method described in ISO 16014-1, -2, -4, issues of 2003. The specifics according to the mentioned ISO standards are as follows: the solvent is 1,2,4-trichlorobenzene (TCB), temperature of apparatus and solutions 135°C and as concentration detector a PolymerChar (Valencia, Paterna 46980, Spain) IR-4 infrared detector, capable for use with TCB. A WATERS Alliance 2000 equipped with the following pre-column SHODEX UT-G and separation columns SHODEX UT 806 M (3x) and SHODEX UT 807 (Showa Denko Europe GmbH, Konrad-Zuse-Platz 4, 81829 Muenchen, Germany) connected in series was used.

[0117]   The solvent was vacuum distilled under nitrogen and was stabilized with 0.025% by weight of 2,6-di-tert-butyl-4-methylphenol. The flowrate used was 1 ml/min, the injection volume was 500μl and polymer concentration was in the range of 0.01% < conc. < 0.05% w/w. The molecular weight calibration was established by using monodisperse polystyrene (PS) standards from Polymer Laboratories (now Agilent Technologies, Herrenberger Str. 130, 71034 Boeblingen, Germany) in the range from 580g/mol up to 11600000g/mol and additionally with hexadecane.

[0118]   The calibration curve was then adapted to Polyethylene (PE) by means of the Universal Calibration method (Benoit H., Rempp P. and Grubisic Z., & in J. Polymer Sci., Phys. Ed., 5, 753(1967)). The Mark-Houwing parameters used herefore were for PS: k_{PS}= 0.000121 dl/g, α_{PS}=0.706 and for PE k_{PE}= 0.000406 dl/g, α_{PE}=0.725, valid in TCB at 135°C. Data recording, calibration and calculation was carried out using NTGPC_Control_V6.02.03 and NTGPC_V6.4.24 (hs GmbH, Hauptstraße 36, D-55437 Ober-Hilbersheim, Germany) respectively.

[0119]   **Melt flow index**

[0120]   Determined according to ISO 1133 at 190°C with the specified load.

[0121]　　　**Long Chain Branching index (LCBI)**

[0122]　　　The LCB index corresponds to the branching factor g', measured for a molecular weight of 10^6 g/mol. The branching factor g', which allows determining long-chain branches at high Mw, was measured by Gel Permeation Chromatography (GPC) coupled with Multi-Angle Laser-Light Scattering (MALLS). The radius of gyration for each fraction eluted from the GPC (as described above but with a flow-rate of 0.6 ml/min and a column packed with 30μm particles) is measured by analyzing the light scattering at the different angles with the MALLS (detector Wyatt Dawn EOS, Wyatt Technology, Santa Barbara, Calif.). A laser source of 120mW of wavelength 658nm was used. The specific index of refraction was taken as 0.104 ml/g. Data evaluation was done with Wyatt ASTRA 4.7.3 and CORONA 1.4 software. The LCB Index is determined as described in the following.

[0123]　　　The parameter g' is the ratio of the measured mean square radius of gyration to that of a linear polymer having the same molecular weight. Linear molecules show a g' value of 1, while values less than 1 indicate the presence of LCB. Values of g' as a function of mol. weight, M, were calculated from the equation:

$$g'(M) = <Rg^2>_{sample,M} / <Rg^2>_{linear\ ref.,M}$$

where $<Rg^2>$, M is the root-mean-square radius of gyration for the fraction of mol. weight M.

[0124]　　　The radius of gyration for each fraction eluted from the GPC (as described above but with a flow-rate of 0.6 ml/min and a column packed with 30μm particles) is measured by analyzing the light scattering at the different angles. Therefore, from this MALLS setup it is possible to determine mol. weight M and $<Rg^2>_{sample,M}$ and to define a g' at a measured M = 10^6 g/mol. The $<Rg^2>_{linear\ ref.,M}$ is calculated by the established relation between radius-of-gyration and molecular weight for a linear polymer in solution (Zimm and Stockmayer WH 1949)) and confirmed by measuring a linear PE reference with the same apparatus and methodology described.

[0125]　　　The same protocol is described in the following documents.

Zimm BH, Stockmayer WH (1949) *The dimensions of chain molecules containing branches and rings*. J Chem Phys 17

Rubinstein M., Colby RH. (2003), *Polymer Physics*, Oxford University Press

[0126]　　　**Comonomer content**

[0127]　　　The comonomer content is determined by means of IR in accordance with ASTM D 6248 98, using an FT-IR spectrometer Tensor 27 from Bruker, calibrated with a chemometric model for determining ethyl- or butyl- side-chains in PE for butene or hexene as

comonomer, respectively. The result is compared to the estimated comonomer content derived from the mass-balance of the polymerization process and was found to be in agreement.

[0128] <u>Swell ratio</u>

[0129] The swell-ratio of the studied polymers is measured utilizing a capillary rheometer, Göttfert Rheotester2000 and Rheograph25, at T = 190°C, equipped with a commercial 30/2/2/20 die (total length 30 mm, Active length=2 mm, diameter = 2 mm, L/D=2/2 and 20° entrance angle) and an optical device (laser-diod from Göttfert) for measuring the extruded strand thickness. Sample is molten in the capillary barrel at190°C for 6 min and extruded with a piston velocity corresponding to a resulting shear-rate at the die of 1440 s^{-1}.

[0130] The extrudate is cut (by an automatic cutting device from Göttfert) at a distance of 150 mm from the die-exit, at the moment the piston reaches a position of 96 mm from the die-inlet. The extrudate diameter is measured with the laser-diod at a distance of 78 mm from the die-exit, as a function of time. The maximum value corresponds to the $D_{extrudate}$. The swell-ratio is determined from the calculation:

$$SR = (D_{extrudate}-D_{die})100\%/D_{die}$$

[0131] where D_{die} is the corresponding diameter at the die exit, measured with the laser-diode.

[0132] <u>Notched Tensile Impact Test AZK</u>

[0133] The tensile-impact strength is determined using ISO 8256:2004 with type 1 double notched specimens according to method A. The test specimens (4 x 10 x 80 mm) are cut from a compression molded sheet which has been prepared according ISO 1872-2 requirements (average cooling rate 15 K/min and high pressure during cooling phase). The test specimens are notched on two sides with a 45° V-notch. Depth is 2 ± 0.1 mm and curvature radius on notch dip is 1.0 ± 0.05 mm.

[0134] The free length between grips is 30 ± 2 mm. Before measurement, all test specimens are conditioned at a constant temperature of -30°C over a period of from 2 to 3 hours. The procedure for measurements of tensile impact strength including energy correction following method A is described in ISO 8256.

[0135] <u>Environmental stress cracking resistance according to full notch creep test (FNCT)</u>

[0136] The environmental stress cracking resistance of polymer samples is determined in accordance to international standard ISO 16770 (FNCT) in aqueous surfactant solution. From the polymer sample a compression moulded 10 mm thick sheet has been prepared. The bars with squared cross section (10x10x100 mm) are notched using a razor blade on four sides

perpendicularly to the stress direction. A notching device described in M. Fleissner in Kunststoffe 77 (1987), pp. 45 is used for the sharp notch with a depth of 1.6 mm.

[0137] The load applied is calculated from tensile force divided by the initial ligament area. Ligament area is the remaining area = total cross-section area of specimen minus the notch area. For an FNCT specimen: 10x10 mm² - 4 times - of trapezoid notch area = 46.24 mm² (the remaining cross-section for the failure process / crack propagation). The test specimen is loaded with standard condition suggested by the ISO 16770 with constant load of 4 MPa at 80°C in a 2% (by weight) water solution of non-ionic surfactant ARKOPAL N100. Time until rupture of test specimen is detected.

[0138] Example 1

[0139] Preparation of the spherical catalyst support

[0140] A magnesium chloride and alcohol adduct containing about 3 mols of alcohol was prepared following the method described in example 2 of USP 4,399,054, but working at a velocity of 2000 RPM instead of 10000 RPM.

[0141] The so obtained adduct was dealcoholated up to an amount of alcohol of 25% wt via a thermal treatment, under nitrogen stream, over a temperature range of 50-150°C.

[0142] Preparation of the solid catalyst component

[0143] Into a 2 L four-necked round flask, purged with nitrogen, 1 L of $TiCl_4$ was introduced at 0°C. Then, at the same temperature, 70 g of a spherical $MgCl_2$/EtOH adduct containing 25% wt of ethanol and prepared as described above were added under stirring. The temperature was raised to 130 °C in 3 hours and maintained for 60 minutes. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off. Fresh $TiCl_4$ was added up to 1 L total volume and the treatment at 130°C for 60 minutes was repeated. After settling and siphoning, the solid residue was then washed five times with hexane at 50°C and two times with hexane at 25 °C and dried under vacuum at 30 °C.

[0144] Into a 2 L four-necked glass reactor provided with stirrer, 812 cc of hexane at 10°C and whilst stirring 50 g of the catalyst component prepared as described above were introduced at 10°C. Keeping constant the internal temperature, 15 g of tri-n-octylaluminum (TNOA) in hexane (about 80 g/l) and an amount of cyclohexylmethyl-dimethoxysilane (CMMS) such as to have molar ratio TNOA/CMMS of 50, were slowly introduced into the reactor and the temperature was maintained to 10°C. After 10 minutes stirring, a total amount of 65 g of propylene were introduced into the reactor at the same temperature in 6.5 hours at constant rate. Then, the whole content was filtered and washed three times with hexane at a temperature of 30 °C (100 g/l). After drying the resulting pre-polymerized catalyst (A) was analyzed

and found to contain 55% wt of polypropylene, 2.0% wt Ti, 9.85% wt Mg and 0.31% wt Al.

[0145] About 100 g of the solid prepolymerized catalyst prepared as described above were charged in a glass reactor purged with nitrogen and slurried with 1.0 L of heptane at 50°C.

[0146] Then, ethylacetate (EAA) and tetrahydrofuran (CE) were carefully added dropwise (in 60') in such an amount to have a molar ratio of 4 between Mg/EAA and 4 between Mg and CE.

[0147] The slurry was kept under stirring for 1.5 h still having 50°C as internal temperature. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off. The solid was washed under stirring one time adding anhydrous heptane at 50°C up to 1 L of volume and then the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off. Then the volume was restored to 1 L with anhydrous heptane and the temperature was raised up to 85 °C and maintained under stirring for 2 hours. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

[0148] The solid was washed 3 times with anhydrous hexane (3 x 1000 mL) at 25°C, recovered, dried under vacuum and analyzed and the resulting EAA/CE molar ratio was found 0.93.

[0149] <u>Polymerization</u>

[0150] 8.9 g/h of the solid catalyst prepared as described above, were fed using 1.1 kg/h of liquid propane to a first stirred precontacting vessel, into which triisobuthyllaluminum (TIBA) and diethylaluminumchloride (DEAC) were also dosed. The weight ratio between trisiobutylaluminum and diethylaluminumchloride was 7:1. The ratio between aluminum alkyls to the Ziegler catalyst was 5:1. The first precontacting vessel was kept at 50°C with an average residence time of 100 minutes. The catalyst suspension of the first precontacting vessel was continuously transferred to a second stirred precontacting vessel, which was operated with an average residence time of 100 minutes and kept also at 50°C. The catalyst suspension was then transferred continuously to fluidized-bed reactor (FBR) (1) via line (10).

[0151] In the first reactor ethylene was polymerized using H_2 as molecular weight regulator and in the presence of propane as inert diluent. 48 kg/h of ethylene and 130 g/h of hydrogen were fed to the first reactor via line 9. No comonomer was fed to the first reactor.

[0152] The polymerization was carried out at a temperature of 80°C and at a pressure of 2.8 MPa. The polymer obtained in the first reactor was discontinuously discharged via line 11, separated from the gas into the gas/solid separator 12, and reintroduced into the second gas-phase reactor via line 14.

[0153]   The polymer produced in the first reactor had a melt index MIE of about 12 g/10 min and a density of 0.965 g/cm³.

[0154]   The second reactor was operated under polymerization conditions of about 85°C, and a pressure of 2.4 MPa. The riser has an internal diameter of 200 mm and a length of 19 m. The downcomer has a total length of 18 m, an upper part of 5 m with an internal diameter of 300 mm and a lower part of 13 m with an internal diameter of 150 mm. In order to broaden the molecular weight distribution of the final ethylene polymer, the second reactor was operated by establishing different conditions of monomers and hydrogen concentration within the riser 32 and the downcomer 33. This is achieved by feeding via line 52, 330 kg/h of a liquid stream (liquid barrier) into the upper part of the downcomer 33. Said liquid stream has a composition different from that of the gas mixture present in the riser. Said different concentrations of monomers and hydrogen within the riser, the downcomer of the second reactor and the composition of the liquid barrier are indicated in Table 1. The liquid stream of line 52 comes from the condensation step in the condenser 49, at working conditions of 48°C and 2.5 MPa, wherein a part of the recycle stream is cooled and partially condensed. As shown in the figure, a separating vessel and a pump are placed, in the order, downstream the condenser 49. The monomers to the downcomer were fed in 3 positions (lines 46). In dosing point 1, located just below the barrier, 14 kg/h of ethylene and 1.22 kg/h of 1-hexene were introduced. In dosing point 2, located 2.3 meters below dosing point 1, 3 kg/h of ethylene were introduced. In dosing point 3, located 4 meters below dosing point 2, 3 kg/h of ethylene were introduced. In each of the 3 dosing points, a liquid taken from stream 52 was additionally fed in ratio to ethylene of 1:1. 5 kg/h of propane, 26 kg/h of ethylene and 30 g/h of hydrogen were fed through line 45 into the recycling system.

[0155]   The final polymer was discontinuously discharged via line 54.

[0156]   The polymerization process in the second reactor produced relatively high molecular weight polyethylene fractions. In Table 1 the properties of the final product are specified. It can be seen that the melt index of the final product is decreased as compared to the ethylene resin produced in the first reactor, showing the formation of high molecular weight fractions in the second reactor.

[0157]   The first reactor produced around 50 % by weight (split wt %) of the total amount of the final polyethylene resin produced by both first and second reactors.

[0158]   The comonomer (hexene-1) amount was of about 1.2% by weight.

[0159]   Comparative Example 1

[0160]   The polymer of this comparative example is a polyethylene composition produced in gas phase with a chromium-containing catalyst and sold with trademark Lupolen 4261AG UV 60005 by LyondellBasell.

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Table 1

	Ex. 1	Comp. 1
Operative conditions first reactor		
H₂/C₂H₄ Molar ratio	1.4	-
C₂H₄%	10.5	-
Density of A) (g/cm³)	0.965	
MIE [2.16 kg] of A) (g/10 min.)	12	
Split (wt.%)	50	-
Operative conditions second reactor		
H₂/C₂H₄ Molar ratio riser	0.29	-
C₂H₄% riser	9.9	-
C₆H₁₂ %riser	0.39	-
H₂/C₂H₄ Molar ratio downcomer	0.010	-
C₂H₄% downcomer	3.2	-
C₆H₁₂ % downcomer	0.52	-
H₂/C₂H₄ Molar ratio barrier	0.008	-
C₂H₄% barrier	6.5	-
C₆H₁₂ % barrier	0.59	-
Final Polymer properties		
MIP [5 kg] (g/10 min.)	0.28	0.30
MIF [21.6 kg] (g/10 min.)	8.16	6.1
MIF/MIP	29.14	20.1
Density (g/cm³)	0.9485	0.9452
Swell ratio (%)	186	202
Mw (g/mol)	383,680	358,112
Mz (g/mol)	2,396,480	3,911,139
Mw/Mn	32.1	21.1
Mz/Mw	6.2	11
LCBI	0.77	0.90
Mz/Mw*LCBI	4.8	9.9
Comonomer content IR (% by weight)	1.2	1 (C₆H₁₂)
η₀.₀₂	175,781	156,083
(η₀.₀₂/1000)/LCBI	228	173.425
AZK -30°C (kJ/m²)	147.8	152
FNCT[1] 4 MPa/80°C (hours)	1120	30.4
HMW COPO Index	5.1	29.5

Notes: C_2H_4 = ethylene; C_6H_{12} = hexene; [1]aqueous solution of 2% Arkopal N100

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A polyethylene composition comprising:

    A) 30 – 70% by weight of an ethylene homopolymer or copolymer with density equal to or greater than 0.960 g/cm^3 and melt flow index MIE at 190°C with a load of 2.16 kg, according to ISO 1133, of 2 to 20 g/10 min.;

    B) 30 – 70% by weight of an ethylene copolymer having a MIE value lower than the MIE value of A), or lower than 0.5 g/10 min.,

    said composition having the following features:

    1) density from 0.940 to 0.955 g/cm^3, determined according to ISO 1183 at 23°C;

    2) ratio MIF/MIP from 12 to 40, where MIF is the melt flow index at 190°C with a load of 21.60 kg, and MIP is the melt flow index at 190°C with a load of 5 kg, both determined according to ISO 1133-1;

    3) Mz from 500,000 to 3,500,000 g/mol, where Mz is the z-average molecular weight, measured by GPC;

    4) $\eta_{0.02}$ from 80,000 to 300,000 Pa.s, wherein $\eta_{0.02}$ is the complex shear viscosity at an angular frequency of 0.02 rad/s, measured with dynamic oscillatory shear in a plate-plate rotational rheometer at a temperature of 190°C;

    5) HMWcopo index from 1 to 15;

        wherein the HMWcopo index is determined according to the following formula:
        HMWcopo = $(\eta_{0.02} \times t_{maxDSC})/(10^5)$

where $\eta_{0.02}$ is the complex shear viscosity of the melt in Pa.s, measured at a temperature of 190°C, in a parallel-plate rheometer under dynamic oscillatory shear mode with an applied angular frequency of 0.02 rad/s; the t_{maxDSC} is the time, in minutes, required to reach the maximum value of heat flow of crystallization at a temperature of 124 °C under quiescent conditions, measured in isothermal mode in a differential scanning calorimetry apparatus;

6) Mz/Mw*LCBI lower than 6.4, wherein LCBI is the ratio of the measured mean-square radius of gyration Rg, measured by GPC-MALLS, to the mean-square radius of gyration for a linear PE having the same molecular weight at a mol. weight of 1,000,000 g/mol.

2. The polyethylene composition of claim 1, consisting of or comprising one or more ethylene copolymers.

3. The polyethylene composition of claims 1 or 2, obtained by using a Ziegler-Natta polymerization catalyst.

4. The polyethylene composition of claim 3, wherein the Ziegler-Natta polymerization catalyst comprises the product of reaction of:

A) a solid catalyst component comprising Ti, Mg, chlorine and one internal electron donor ED selected from esters of aliphatic monocarboxylic acids (EAA) and another internal donor ED^I selected from cyclic ethers (CE) in an amount such that the EAA/CE molar ratio ranges from 0.02 to less than 20;

B) an organo-Al compound; and optionally

C) an external electron donor compound.

5. The polyethylene composition of claim 1, having at least one of the following additional features:

- MIF from 4 to 15 g/10min.;

- ratio $(\eta_{0.02}/1000)/$ LCBI, which is between $\eta_{0.02}$ divided by 1000 and LCBI, equal to or greater than 150;

- comonomer content equal to or less than 2% by weight, with respect to the total weight of the composition;

- LCBI equal to or greater than 0.65.

6. The polyethylene composition of claim 1, comprising:

A) 40 – 60% by weight of an ethylene homopolymer or copolymer with density equal to or greater than 0.960 g/cm^3 and melt flow index MIE at 190°C with a load of 2.16 kg, according to ISO 1133, of 2 to 20 g/10 min.;

B) 40 – 60% by weight of an ethylene copolymer having a MIE value lower than the MIE value of A), than 0.5 g/10 min.

7. Manufactured articles comprising the polyethylene composition of claim 1.

8. Manufactured articles according to claim 7, in form of blow-molded hollow articles.

9. Process for preparing the polyethylene composition of claim 1, wherein all the polymerization steps are carried out in the presence of a Ziegler-Natta polymerization catalyst supported on $MgCl_2$.

10. The process of claim 9, comprising the following steps, in any mutual order:

a) polymerizing ethylene, optionally together with one or more comonomers, in a gas-phase reactor in the presence of hydrogen;

b) copolymerizing ethylene with one or more comonomers in another gas-phase reactor in the presence of an amount of hydrogen less than step a);

where in at least one of said gas-phase reactors the growing polymer particles flow upward through a first polymerization zone under fast fluidization or transport conditions, leave said riser and enter a second polymerization zone through which they flow downward under the action of gravity, leave said second polymerization zone and are reintroduced into the first polymerization zone, thus establishing a circulation of polymer between said two polymerization zones.
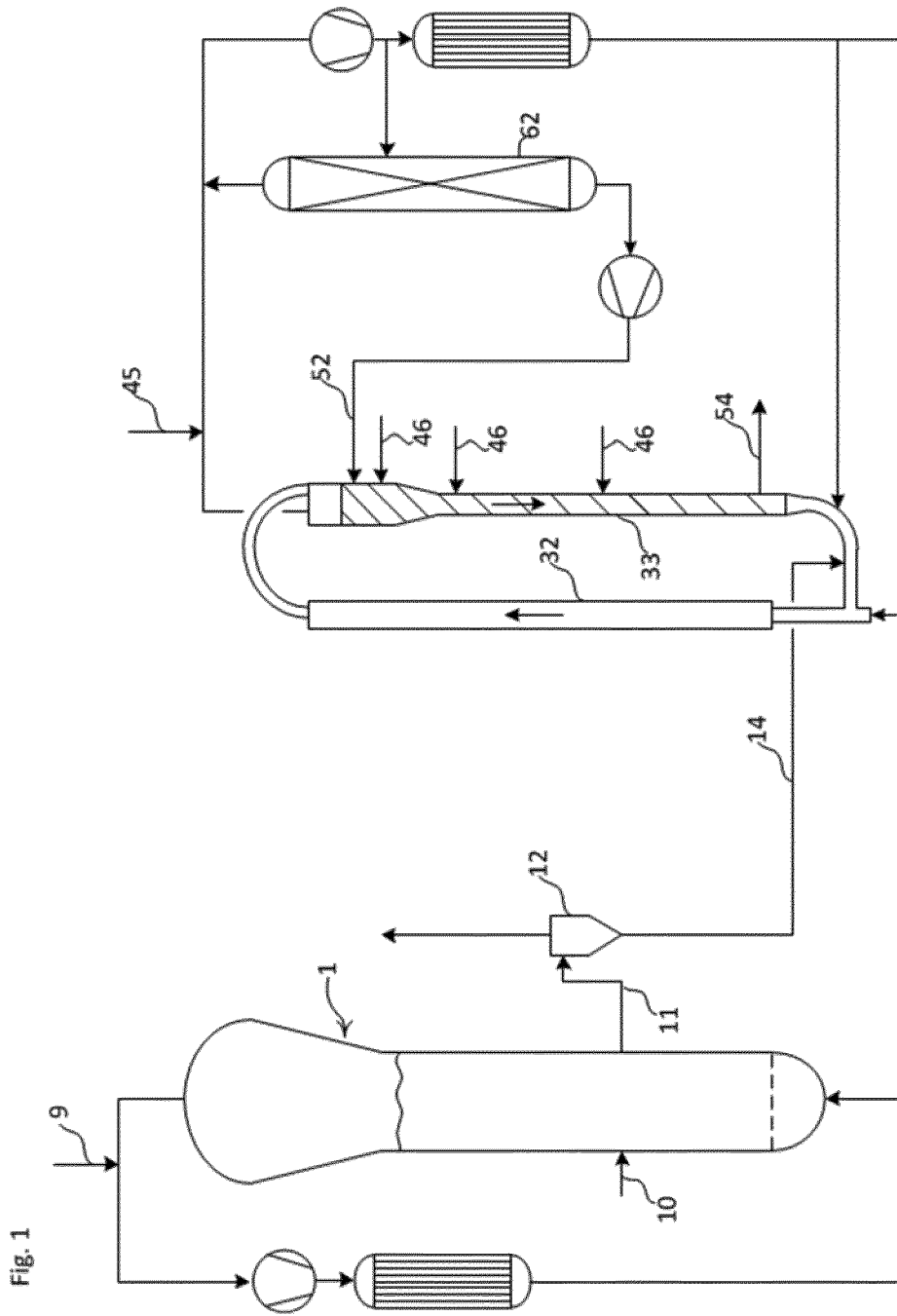
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Fig. 1

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1

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