

**Modified polyethylene having improved hydrostatic pressure resistance and  
slow crack growth resistance**

**5 Field of the Invention**

The present invention relates to a precursor polyethylene composition comprising an ethylene-hexene copolymer and a modifier, to a process of forming a thermoplastic polyethylene composition from said precursor polyethylene composition, to the  
10 thermoplastic polyethylene composition thus obtained, to articles comprising said thermoplastic polyethylene composition and to the use of a modifier for increasing the hydrostatic pressure resistance and/or slow crack growth resistance of polyethylene pipes.

**Background to the Invention**

15 Polyethylene has long been one of the most commonly employed materials for producing pipes. For pipe applications, there are extremely demanding requirements with regard the long term performance of the pipes, with properties such as hydrostatic pressure resistance, both at low and high temperature, as well as slow crack growth resistance key to avoiding  
20 potential catastrophic failures of key infrastructure, affecting large numbers of people and businesses.

Highly engineered polyethylene compositions are known in the art for addressing these issues, although there is plenty of scope to improve upon these known examples, both in  
25 terms of improving performance and also avoiding unnecessarily complex and/or expensive processes.

WO 03/085044 A1 achieves improved NCTL stress crack resistance through bimodal polymer design.

30 EP 3 293 208 A1 also achieves improved pipe properties for bimodal ethylene-butene copolymers.

The use of modifiers in the field of polyethylene pipes is known, although the effect of such  
35 modifiers on long term pipe properties is not. Furthermore, it is well-known that crosslinking polyethylene for pipes may result in undesirable lumpiness/surface roughness.

WO 2019/219902 A1 discloses the use of a rheology modifier for improving rheological properties of polyolefins without affecting the mechanical properties.

- 5 As such, there is still progress to be made in providing polyethylene compositions having improved hydrostatic pressure resistance and/or slow crack growth resistance in combination with good surface appearance and beneficial rheological properties.

### Summary

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It is the finding of the present invention that a modifier having two or more ethylenically unsaturated groups can be used to improve various pipe properties, including hydrostatic pressure resistance and/or slow crack growth resistance.

- 15 Therefore, in a first aspect, the present invention is directed to a precursor polyethylene composition (PPC), comprising:
- a) an ethylene-hexene copolymer (PE) having:
    - i) melt flow rate (MFR<sub>5</sub>), determined according to ISO 1133 at 190 °C and 5.0 kg, in the range from 0.10 to 1.00 g/10 min;
    - 20 ii) a 1-hexene content, determined according to quantitative <sup>13</sup>C-NMR spectroscopy, in the range from 0.8 to 2.0 wt.-%; and
    - iii) a molecular weight distribution (Mw/Mn), determined by gel permeation chromatography (GPC), in the range from 28.5 to 40.0, and
  - b) a modifier (M) having two or more ethylenically unsaturated groups,
- 25 wherein the ethylene-hexene copolymer (PE) and the modifier (M) are reactive to form a thermoplastic polyethylene composition at a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg.

- In a second aspect, the present invention is directed to a process for forming a thermoplastic polyethylene composition (TPC), comprising the steps of:
- 30 a) providing a precursor polyethylene composition (PPC) according to the first aspect;

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- b) heating the precursor polyethylene composition (PPC) to a temperature of 180 to 300 °C;  
and  
c) subjecting the precursor polyethylene composition (PPC) to a specific energy of equal to  
or more than 0.15 kWh/kg, thereby obtaining the thermoplastic polyethylene  
composition (TPC).

In a third aspect, the present invention is directed to a thermoplastic polyethylene composition (TPC) obtainable, more preferably obtained, by the process of the second aspect.

In a fourth aspect, the present invention is directed to an article comprising the thermoplastic polyethylene composition (TPC) of the third aspect, which is selected from a pipe, film or blow moulded article.

In a final aspect, the present invention is directed to a use of a modifier having two or more ethylenically unsaturated groups in a precursor polyethylene composition that comprises a polyethylene and the modifier and is preferably free from radical initiators, for increasing the hydrostatic pressure resistance and/or slow crack growth resistance of a pipe formed from a thermoplastic polyethylene composition obtained by exposing the precursor polyethylene composition to a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

### Definitions

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although, any methods and materials similar or equivalent to those described herein can be used in practice for testing of the present invention, the preferred materials and methods are described herein. In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below.

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Unless clearly indicated otherwise, use of the terms “a,” “an,” and the like refers to one or more.

In the following, amounts are given in % by weight (wt.-%) unless it is stated otherwise.

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An ethylene homopolymer is a polymer that essentially consists of ethylene monomer units. Due to impurities especially during commercial polymerization processes, an ethylene homopolymer can comprise up to 0.1 mol-% comonomer units, preferably up to 0.05 mol-% comonomer units and most preferably up to 0.01 mol-% comonomer units.

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An ethylene copolymer is a copolymer of ethylene monomer units and comonomer units in an amount of at least 0.1 mol-%, preferably selected from C<sub>3</sub>-C<sub>8</sub> alpha-olefins. Ethylene copolymers can comprise comonomer units from one or more comonomers different in their amounts of carbon atoms.

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In the context of the present invention, an ethylene-hexene copolymer is a copolymer that consists essentially of only ethylene monomers and hexene comonomers.

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Specific energy is the energy introduced into the polyethylene composition, usually by means of kinetic energy generated through shear force.

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Shearing forces in general are unaligned forces pushing one part of a body in one specific direction, and another part of the body in the opposite direction. In the context of the present invention, shearing forces are usually induced on the polyethylene composition by the screw or screws in the compounder such as the extruder.

The present invention will now be described in more detail.

**Detailed Description****Precursor polyethylene composition (PPC)**

- 5 In a first aspect, the present invention is directed to a precursor polyethylene composition (PPC), comprising:
- a) an ethylene-hexene copolymer (PE), and
  - b) a modifier (M).
- 10 The precursor polyethylene composition (PPC) preferably contains less than 2.0 wt.-% of radical initiators, more preferably less than 1.0 wt.-% of radical initiators, most preferably is free from radical initiators.

- Furthermore, the ethylene-hexene copolymer (PE) and the modifier (M) are reactive to form
- 15 a thermoplastic polyethylene composition at a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg.

- It is preferred that the above reaction conditions, under which the ethylene-hexene copolymer (PE) and the modifier (M) are reactive to form the thermoplastic polyethylene
- 20 composition, are in a compounder, suitably an extruder. Said reaction conditions are therefore not applied through an additional processing step, for example an infrared heating curing step.

- Preferably the temperature for reacting the ethylene-hexene copolymer (PE) and the modifier
- 25 (M) is in the range of from 180 to 300°C, more preferably in the range of from 200 to 285°C and most preferably in the range of from 220 to 280°C.

- Preferably, the specific energy for reacting the ethylene-hexene copolymer (PE) and the modifier (M) is in the range of from 0.15 kWh/kg to 0.50 kWh/kg, more preferably in the
- 30 range of from 0.20 kWh/kg to 0.40 kWh/kg and most preferably in the range of from 0.20 kWh/kg to 0.30 kWh/kg.

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The specific energy is preferably introduced into the precursor polyethylene composition (PPC) as kinetic energy, such as by means of shearing forces.

5 Thereby, the shearing forces to be applied to obtain a certain specific energy can depend on the density and viscosity of the ethylene-hexene copolymer (PE). The lower the enthalpy and thus, the density and the lower the viscosity, the lower is the amount of shearing forces, which need to be applied to obtain a certain specific energy.

10 It has been found in the present invention that a minimum specific energy of 0.15 kWh/kg has to be applied in order to initiate the reactivity of the modifier (M).

A specific energy higher than 0.50 kWh/kg can result in chain scissions of the polymer chains of the ethylene-hexene copolymer (PE).

15 The temperature and specific energy for reacting the precursor polyethylene composition (PPC) are usually applied during the compounding step of the precursor polyethylene composition (PPC). The compounding step usually is conducted in a compounder such as a melt mixer or an extruder.

20 The temperature is preferably applied by extruding the precursor polyethylene composition (PPC) at an extruding temperature in the above described range.

The specific energy is preferably applied by extruding the precursor polyethylene composition (PPC) at a certain screw speed of the one or two screws of the extruder.

25 Preferably, the modifier (M) is present in an amount in the range from 100 to 1500 ppm, more preferably in the range from 150 to 1200 ppm, yet more preferably in the range from 200 to 1000 ppm, even more preferably in the range from 250 to 800 ppm, most preferably in the range from 300 to 600 ppm, relative to the total weight of the precursor polyethylene composition (PPC).

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The precursor polyethylene composition (PPC) preferably further comprises carbon black (CB) in an amount in the range from 1.0 to 4.0 wt.-%, more preferably in the range from 1.5 to 3.5 wt.-%, yet more preferably in the range from 1.8 to 3.2 wt.-%, even more preferably in the range from 1.9 to 3.0 wt.-%, most preferably in the range from 2.0 to 2.7 wt.-%, relative to the total weight of the precursor polyethylene composition (PPC).

Carbon black (CB) can be added to precursor polyethylene composition (PPC) as such (neat) or in form of so-called master batch (CBMB), in which carbon black, and optionally further additives (A) as defined below, are contained in concentrated form in a carrier polymer.

In addition to the ethylene-hexene copolymer (PE), the modifier (M), and the carbon black (CB), the precursor polyethylene composition (PPC) may contain further additives (A).

The skilled practitioner would be able to select suitable additives that are well known in the art.

The additives are preferably selected from pigments (other than carbon black), nucleating agents, antioxidants, UV-stabilizers, anti-scratch agents, mold release agents, acid scavengers, lubricants, anti-static agents, and mixtures thereof.

If radical initiators are present, then the total weight of radical initiators contribute to the total weight of further additives (A).

It is understood that the content of additives includes any carrier polymers used to introduce the additives or the carbon black (if present) to the precursor polyethylene composition (PPC), i.e. masterbatch carrier polymers. An example of such a carrier polymer would be a high-density polyethylene in the form of powder or pellets.

If present, additives (A) are present in an amount in the range from 0.01 to 7.0 wt.-% relative to the total weight of the precursor polyethylene composition (PPC).

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In one particularly preferred embodiment, the precursor polyethylene composition (PPC) comprises, more preferably consists of:

- a) an amount in the range from 88.850 to 99.990 wt.-%, more preferably in the range from 89.380 to 99.985 wt.-%, yet more preferably in the range from 89.700 to 99.980 wt.-%, even more preferably in the range from 89.920 to 99.975 wt.-%, most preferably in the range from 90.240 to 97.970 wt.-%, of the ethylene-hexene copolymer (PE),
- b) an amount in the range from 100 to 1500 ppm, more preferably in the range from 150 to 1200 ppm, yet more preferably in the range from 200 to 1000 ppm, even more preferably in the range from 250 to 800 ppm, most preferably in the range from 300 to 600 ppm, of the modifier (M),
- c) optionally, an amount in the range from 1.0 to 4.0 wt.-%, more preferably in the range from 1.5 to 3.5 wt.-%, yet more preferably in the range from 1.8 to 3.2 wt.-%, even more preferably in the range from 1.9 to 3.0 wt.-%, most preferably in the range from 2.0 to 2.7 wt.-%, of carbon black (CB), and
- d) optionally, an amount in the range from 0.01 to 7.0 wt.-%, of additives (A).

In one alternative, the precursor polyethylene composition (PPC) comprises, more preferably consists of:

- a) an amount in the range from 88.850 to 98.990 wt.-%, more preferably in the range from 89.380 to 98.485 wt.-%, yet more preferably in the range from 89.700 to 98.180 wt.-%, even more preferably in the range from 89.920 to 98.075 wt.-%, most preferably in the range from 90.240 to 97.970 wt.-%, of the ethylene-hexene copolymer (PE),
- b) an amount in the range from 100 to 1500 ppm, more preferably in the range from 150 to 1200 ppm, yet more preferably in the range from 200 to 1000 ppm, even more preferably in the range from 250 to 800 ppm, most preferably in the range from 300 to 600 ppm, of the modifier (M),
- c) an amount in the range from 1.0 to 4.0 wt.-%, more preferably in the range from 1.5 to 3.5 wt.-%, yet more preferably in the range from 1.8 to 3.2 wt.-%, even more preferably in the range from 1.9 to 3.0 wt.-%, most preferably in the range from 2.0 to 2.7 wt.-%, of carbon black (CB), and
- d) optionally, an amount in the range from 0.01 to 7.0 wt.-%, of additives (A).

In another alternative, the precursor polyethylene composition (PPC) comprises, more preferably consists of:

- a) an amount in the range from 92.850 to 99.990 wt.-%, more preferably in the range from 92.880 to 99.985 wt.-%, yet more preferably in the range from 92.900 to 99.980 wt.-%, even more preferably in the range from 92.920 to 99.975 wt.-%, most preferably in the range from 92.940 to 97.970 wt.-%, of the ethylene-hexene copolymer (PE),
- b) an amount in the range from 100 to 1500 ppm, more preferably in the range from 150 to 1200 ppm, yet more preferably in the range from 200 to 1000 ppm, even more preferably in the range from 250 to 800 ppm, most preferably in the range from 300 to 600 ppm, of the modifier (M), and
- c) optionally, an amount in the range from 0.01 to 7.0 wt.-%, of additives (A).

The precursor polyethylene composition (PPC) is suitably produced by blending the ethylene-hexene copolymer (PE) the modifier (M) and optionally further additives (A) and/or carbon black (CB) as described above or below.

The blending can be conducted by mixing the components e.g. by dry-blending introducing the blended composition into a compounder such as a melt mixer or an extruder.

The blending can also be conducted within the compounder such as a melt mixer or extruder by feeding the components into the compounder, e.g. in different feeding ports of an extruder.

The individual components of the precursor polyethylene composition are described in more detail below.

#### **Ethylene-hexene copolymer (PE)**

One essential component of the precursor polyethylene composition (PPC) is the ethylene-hexene copolymer (PE).

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The ethylene-hexene copolymer (PE) consists essentially of ethylene monomer units and 1-hexene comonomer units.

5 The ethylene-hexene copolymer (PE) preferably has a density, determined according to ISO 1183-1:2004, in the range from 950 to 975 kg/m<sup>3</sup>, more preferably in the range from 954 to 970 kg/m<sup>3</sup>, most preferably in the range from 958 to 965 kg/m<sup>3</sup>.

10 The ethylene-hexene copolymer (PE) has a 1-hexene content, determined according to quantitative <sup>13</sup>C-NMR spectroscopy, in the range from 0.8 to 2.0 wt.-%, more preferably in the range from 0.8 to 1.8 wt.-%, most preferably in the range from 0.8 to 1.5 wt.-%.

15 The ethylene-hexene copolymer (PE) has a melt flow rate (MFR<sub>5</sub>), determined according to ISO 1133 at 190 °C and 5.0 kg, in the range from 0.10 to 1.00 g/10 min, more preferably in the range from 0.12 to 0.50 g/10 min, most preferably in the range from 0.15 to 0.30 g/10 min.

20 The ethylene-hexene copolymer (PE) preferably has a melt flow rate (MFR<sub>21</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg, in the range from 3.0 to 30.0 g/10 min, more preferably in the range from 4.0 to 20.0 g/10 min, most preferably in the range from 5.0 to 15.0 g/10 min.

25 The ethylene-hexene copolymer (PE) preferably has a flow rate ratio (FRR<sub>21/5</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg / 5 kg, in the range from 25 to 40, more preferably in the range from 27 to 37, most preferably in the range from 29 to 35.

30 The ethylene-hexene copolymer (PE) preferably has a viscosity at a shear stress of 747 Pa (eta<sub>747</sub>), determined according to the measurement method given in the determination methods, in the range from 400 to 700 kPa.s, more preferably in the range from 420 to 670 kPa.s, most preferably in the range from 440 to 650 kPa.s.

The ethylene-hexene copolymer (PE) preferably has a zero shear viscosity, determined according to the measurement method given in the determination methods, in the range from

800 to 3000 kPa.s, more preferably in the range from 900 to 2500 kPa.s, most preferably in the range from 1000 to 2000 kPa.s

- 5 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{5/200}$ ), determined according to the measurement method given in the determination methods, in the range from 40 to 60, more preferably in the range from 42 to 55, most preferably in the range from 44 to 50.

- 10 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{0/50}$ ), determined according to the measurement method given in the determination methods, in the range from 15 to 45, more preferably in the range from 20 to 40, most preferably in the range from 25 to 37.

- 15 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{0/100}$ ), determined according to the measurement method given in the determination methods, in the range from 50 to 100, more preferably in the range from 55 to 95, most preferably in the range from 60 to 90.

- 20 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{1/100}$ ), determined according to the measurement method given in the determination methods, in the range from 15 to 40, more preferably in the range from 20 to 35, most preferably in the range from 24 to 32.

- 25 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{2.7/210}$ ), determined according to the measurement method given in the determination methods, in the range from 55 to 85, more preferably in the range from 60 to 80, most preferably in the range from 65 to 75.

- 30 The ethylene-hexene copolymer (PE) preferably has a shear thinning index ( $SHI_{5/300}$ ), determined according to the measurement method given in the determination methods, in the range from 100 to 150, more preferably in the range from 110 to 145, most preferably in the range from 120 to 140.

The ethylene-hexene copolymer (PE) preferably has a crossover frequency, determined according to the measurement method given in the determination methods, in the range from 0.70 to 1.10 rad/s, more preferably in the range from 0.70 to 1.05 rad/s, most preferably in the range from 0.70 to 1.00 rad/s.

The ethylene-hexene copolymer (PE) preferably has a crossover modulus ( $G^*c$ ), determined according to the measurement method given in the determination methods, in the range from 28.0 to 32.0 kPa, more preferably in the range from 28.5 to 31.5 kPa, most preferably in the range from 29.0 to 31.0 kPa.

The ethylene-hexene copolymer (PE) preferably has a rheological polydispersity index (PI), determined according to the measurement method given in the determination methods, in the range from 3.00 to 3.60, more preferably in the range from 3.15 to 3.55, most preferably in the range from 3.30 to 3.50.

The ethylene-hexene copolymer (PE) has a molecular weight distribution ( $M_w/M_n$ ), determined by gel permeation chromatography (GPC), in the range from 28.5 to 40.0, more preferably in the range from 29.0 to 39.0, most preferably in the range from 30.0 to 38.0.

The ethylene-hexene copolymer (PE) preferably has a number average molecular weight ( $M_n$ ), determined according to ISO 16014-4, in the range from 6,000 to 9,000 g/mol, more preferably in the range from 7,000 to 8,700 g/mol, most preferably in the range from 7,500 to 8,500 g/mol.

The ethylene-hexene copolymer (PE) preferably has a weight average molecular weight ( $M_w$ ), determined according to ISO 16014-4, in the range from 200,000 to 300,000 g/mol, more preferably in the range from 220,000 to 280,000 g/mol, most preferably in the range from 240,000 to 270,000 g/mol.

The ethylene-hexene copolymer (PE) preferably has a z-average molecular weight ( $M_z$ ), determined according to ISO 16014-4, in the range from 1,200,000 to 1,900,000 g/mol, more

preferably in the range from 1,300,000 to 1,800,000 g/mol, most preferably in the range from 1,400,000 to 1,700,000 g/mol.

The ethylene-hexene copolymer (PE) can be unimodal, bimodal or multimodal.

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Multimodal resins are frequently used e.g. for the production of pipes due to their favorable physical and chemical properties as e.g. mechanical strength, corrosion resistance and long-term stability. Such compositions are described e.g. in EP 0 739 937 and WO 02/102891.

The term molecular weight used herein generally denotes the weight average molecular weight Mw.

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Usually a polyethylene resin used for pipe or injection moulding applications comprises at least two polyethylene fractions, which have been produced under different polymerization conditions resulting in different weight average molecular weights for the fractions, is

referred to as “multimodal”. The prefix “multi” relates to the number of different polymer fractions the composition is consisting of. Thus, for example, a polyethylene resin consisting of two fractions only is called “bimodal”.

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The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as function of its molecular weight, of such a multimodal polyethylene will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions.

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For example, if a polymer is produced in a sequential multistage process, utilizing reactors coupled in series and using different conditions in each reactor, the polymer fractions produced in the different reactors will each have their own molecular weight distribution and weight average molecular weight. When the molecular weight distribution curve of such a polymer is recorded, the individual curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, usually yielding a curve with two or more distinct maxima.

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Polyethylene resins which include polyethylene fractions, which differ not in their molecular weight but in their comonomer content, are also called "multimodal". A polyethylene resin with two fractions differing in their comonomer content thus are also called "bimodal".

A unimodal polyethylene resin only includes one polyethylene fraction which cannot be differentiated in molecular weight or comonomer content. Usually, unimodal polyethylene resins are polymerized in a single polymerization stage.

It is particularly preferred that the ethylene-hexene copolymer (PE) comprises:

- a) a low molecular weight fraction (PE1) being an ethylene homopolymer; and
- b) a high molecular weight fraction (PE2) being an ethylene-hexene copolymer, wherein the total amount of the low molecular weight fraction (PE1) and the high molecular weight fraction (PE2) is at least 90 wt.-%, relative to the total weight of the ethylene-hexene copolymer (PE), and wherein the ratio of the low molecular weight fraction (PE1) and the high molecular weight fraction (PE2), [PE1]:[PE2], is preferably in the range from 50.5 : 49.5 to 60.0 : 40.0, more preferably in the range from 50.5 : 49.5 to 55.0 : 45.0, most preferably in the range from 50.5 : 49.5 to 53.0 : 47.0.

In addition to the low molecular weight fraction (PE1) and the high molecular weight fraction (PE2), a prepolymer (PE0) may also be present. Such prepolymers are typically produced in order to achieve control of catalyst particle morphology and/or activity in the main polymerization steps (i.e. in the production of PE1 and PE2).

The ethylene-hexene copolymer (PE) can be produced by any process known to the person skilled in the art.

Said processes may employ well-known catalysts for ethylene polymerization, such as Ziegler-Natta catalysts, single site catalysts and chromium catalysts. Preferably a Ziegler-Natta catalyst is employed.

A Ziegler-Natta type catalyst typically used for propylene polymerization and/or copolymerization will be a stereospecific, solid, high yield Ziegler-Natta catalyst component comprising as main components Mg, Ti and Cl. In addition to the solid catalyst component, a

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cocatalyst(s) as well as external donor(s) will generally be used in the polymerization process.

5 The components of the catalyst may be supported on a particulate support, such as inorganic oxide, like silica or alumina, or, usually, a magnesium halide may form the solid support. It is also possible that the catalyst components are not supported on an external support, but the catalyst is prepared by an emulsion-solidification method or by a precipitation method, as is well-known by the man skilled in the art of catalyst preparation.

10 The solid catalyst usually also comprises at least one electron donor (internal electron donor) and optionally aluminium.

Suitable external electron donors used in the polymerization are well known in the art and include ethers, ketones, amines, alcohols, phenols, phosphines and silanes.

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Examples of suitable Ziegler-Natta catalysts and components in the catalysts are described among others in WO87/07620, WO92/21705, WO93/11165, WO93/11166, WO93/19100, WO97/36939, WO98/12234, WO99/33842, WO03/000756, WO03/000757, WO03/000754, WO03/000755, WO2004/029112, EP2610271, WO2012/007430, WO92/19659,

20 WO92/19653, WO92/19658, US4382019, US4435550, US4465782, US4473660, US4560671, US5539067, US5618771, EP45975, EP45976, EP45977, WO95/32994, US4107414, US4186107, US4226963, US4347160, US4472524, US4522930, US4530912, US4532313, US4657882, US4581342, US4657882.

25 The group of single site catalysts comprises of metallocene and non-metallocene catalysts. By conducting polymerization in the presence of a single site polymerization catalyst, optionally in, for example, a solution process, the ethylene-hexene copolymer (PE) as described herein, may be produced. The single site catalyst may suitably be a metallocene catalyst. Such catalysts comprise a transition metal compound that contains a  
30 cyclopentadienyl, indenyl or fluorenyl ligand. The catalyst contains, e.g., two cyclopentadienyl, indenyl or fluorenyl ligands, which may be bridged by a group preferably containing silicon and/or carbon atom(s). Further, the ligands may have substituents, such as

alkyl groups, aryl groups, arylalkyl groups, alkylaryl groups, silyl groups, siloxy groups, alkoxy groups and like. Suitable metallocene compounds are known in the art and are disclosed, among others, in WO-A-97/28170, WO-A-98/32776, WO-A-99/61489, WO-A-03/010208, WO-A-03/051934, WO-A-03/051514, WO-A-2004/085499, EP-A-1752462 and  
5 EP-A-1739103.

Especially, the metallocene compound must be capable of producing polyethylene having sufficiently high molecular weight. Especially it has been found that metallocene compounds having hafnium as the transition metal atom or metallocene compounds comprising an  
10 indenyl or tetrahydroindenyl type ligand often have the desired characteristics. One example of suitable metallocene compounds is the group of metallocene compounds having zirconium, titanium or hafnium as the transition metal and one or more ligands having indenyl structure bearing a siloxy substituent, such as [ethylenebis(3,7-di(tri-  
isopropylsiloxy)inden-1-yl)] zirconium dichloride (both rac and meso), [ethylenebis(4,7-  
15 di(tri-isopropylsiloxy)inden-1-yl)]zirconium dichloride (both rac and meso), [ethylenebis(5-tert-butyltrimethylsiloxy)inden-1-yl)]zirconium dichloride (both rac and meso), bis(5-tert-butyltrimethylsiloxy)inden-1-yl)]zirconium dichloride, [dimethylsilylenenebis(5-tert-butyltrimethylsiloxy)inden-1-yl)] zirconium dichloride (both rac and meso), N-tert-butylamido(dimethyl)( $\eta^5$ -inden-4-yl)silanetitanium dichloride and [ethylenebis(2-  
20 (tert-butyltrimethylsiloxy)inden-1-yl)]zirconium dichloride (both rac and meso).

Another example is the group of metallocene compounds having hafnium as the transition metal atom and bearing a cyclopentadienyl type ligand, such as bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl) dibenzylhafnium,  
25 dimethylsilylenenebis(n-butylcyclopentadienyl)hafnium dichloride (both rac and meso) and bis[1,2,4-tri(ethyl)cyclopentadienyl]hafnium dichloride. Still another example is the group of metallocene compounds bearing a tetrahydroindenyl ligand such as bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride, bis(4,5,6,7-tetrahydroindenyl)hafnium dichloride, ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride, dimethylsilylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride.  
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The single site catalyst typically also comprises an activator. Generally used activators are alumoxane compounds, such as methylalumoxane (MAO), tetraisobutylalumoxane (TIBAO) or hexaisobutylalumoxane (HIBAO). Also boron activators, such as those disclosed in US-A-2007/049711 may be used. The activators mentioned above may be used alone or they  
5 may be combined with, for instance, aluminium alkyls, such as triethylaluminium or triisobutylaluminium.

Depending on the polymerization process, the catalyst may be supported. The support may be any particulate support, including inorganic oxide support, for example, silica, alumina or  
10 titanium, or a polymeric support, for example, a polymeric support comprising styrene or divinylbenzene. When a supported catalyst is used the catalyst needs to be prepared so that the activity of the catalyst does not suffer. Further, any catalyst residues that remain in a final polymer or product shall also not have any negative impact on the key properties such as, e.g., homogeneity, electrical performance or mechanical properties. The catalyst may also  
15 comprise the metallocene compound on solidified alumoxane or it may be a solid catalyst prepared according to emulsion solidification technology. Such catalysts are disclosed, among others, in EP-A- 1539775 or WO-A-03/051934.

Chromium catalysts are previously well known, and for detailed description, see M. P. McDaniel, Advances in Catalysis, Vol. 33 (1985), pp 47-98 and M. P. McDaniel, Ind. Eng. Chem. Res., Vol. 27 (1988), pp 1559-1569. Normally, the chromium catalyst is supported by a carrier, preferably silica. The so-called Phillips catalyst, which is based on chromium trioxide on a silica carrier, is a chromium catalyst suitably used in the invention. The Phillips catalyst is generally produced by activating silica together with a so-called master batch of  
25 chromium trioxide or chromic acetate. When chromic acetate is used it is oxidised to chromium trioxide, so that the end product is the same no matter whether chromium trioxide or chromic acetate is used. The chromium trioxide forms volatile chromic acid, which is evenly distributed on the silica particles. The 6-valent chromium deposited on the silica particles should then be reduced in order to become catalytically active, and this happens  
30 when the chromium comes into contact with the ethylene in the polymerization reactor. Further, another type of chromium catalyst that can be used in the present invention is the so-called chromate-type catalyst. When producing such a catalyst, a chromate compound, such

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as silyl chromate, is deposited on an activated silica carrier. The deposited chromate is reduced by means of an alkoxide, such as an aluminium alkoxide, e.g. diethyl aluminium ethoxide.

- 5 The chromium catalyst, in accordance with the present invention, can be modified by titanation and fluoridation, which is in accordance with the prior art (see, for instance, the Preparation of Catalysts, V. G. Oncelet et al, Elsevier Science Publishers, Amsterdam, 1991, pp 215-227, an article by C. 30 E. Marsden).
- 10 When the ethylene-hexene copolymer (PE) is desired to be a unimodal ethylene-hexene copolymer, it can be produced by a single stage polymerization in a single reactor in a well-known and documented manner. When multimodal (e.g. bimodal) ethylene-hexene copolymer is required, it can be produced e.g. by blending mechanically together two or more separate polymer components or, for example, by in-situ blending during the
- 15 polymerization process of the components. Both mechanical and in-situ blending are well known in the field.

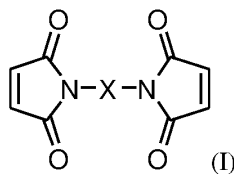
#### **Modifier (M)**

- 20 The other essential component of the precursor polyethylene composition (PPC) is the modifier (M).

In the broadest sense, the modifier (M) may be any suitable modifier having two or more ethylenically unsaturated groups.

25

It is preferred that the modifier (M) has a structure according to formula (I):

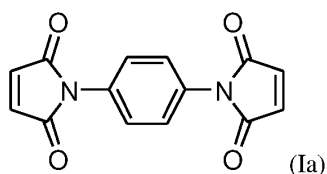


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wherein X is a linking group selected from the group consisting of phenylene and linear or branched C<sub>2</sub> to C<sub>10</sub> alkylene.

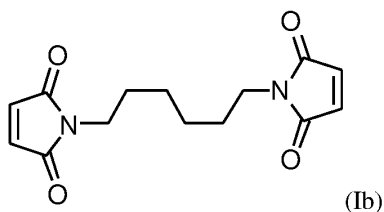
It is particularly preferred that X is selected from the group consisting of 1,4-phenylene and  
5 linear C<sub>4</sub> to C<sub>8</sub> alkylene.

In one embodiment, X is 1,4-phenylene, i.e. the modifier has the structure according to formula (Ia)



10

Most preferably, X is  $-(CH_2)_6-$ , i.e. the modifier has the structure according to formula (Ib)



Since the precursor polyethylene composition (PPC) is preferably free of radical initiators,  
15 the modifier (M) is preferably capable of reacting with the ethylene-hexene copolymer (PE) directly, without being promoted by a radical initiator.

The modifier (M) can be added to the precursor polyethylene composition (PPC) as such (neat) in the amounts as described above or in form of so-called master batch (MB), in which  
20 the modifier (M) is contained in concentrated form in a carrier polymer.

The optional carrier polymer of the rheology modifier does not contribute to the total content of the modifier (M), rather it is assigned to the further additives (A), in the same way as a carbon black masterbatch (CBMB) carrier polymer would be or an additive masterbatch  
25 carrier polymer would be, as described above.

- 20 -

### Process

In a second aspect, the present invention is directed to a process for forming a thermoplastic polyethylene composition (TPC), comprising the steps of:

- 5 a) providing a precursor polyethylene composition (PPC) according to the first aspect;  
b) heating the precursor polyethylene composition (PPC) to a temperature of 180 to 300 °C;  
and  
c) subjecting the precursor polyethylene composition (PPC) to a specific energy of equal to  
or more than 0.15 kWh/kg, thereby obtaining the thermoplastic polyethylene  
10 composition (TPC).

Preferably the temperature of step b) is in the range of from 180 to 300°C, more preferably in the range of from 200 to 285°C and most preferably in the range of from 220 to 280°C.

- 15 Preferably, the specific energy of step c) is in the range of from 0.15 kWh/kg to 0.50 kWh/kg, more preferably in the range of from 0.20 kWh/kg to 0.40 kWh/kg and most preferably in the range of from 0.20 kWh/kg to 0.30 kWh/kg.

The temperature and specific energy for reacting the precursor polyethylene composition  
20 (PPC) are usually applied during the compounding step of the precursor polyethylene composition (PPC). The compounding step usually is conducted in a compounder such as a melt mixer or an extruder.

It is particularly preferred that process steps b) and c) are carried out simultaneously in a  
25 compounder, preferably an extruder selected from a single-screw extruder and a twin-screw extruder.

The compounder preferably is an extruder which more preferably is selected from a single  
screw extruder or a twin screw extruder.

30

In an especially preferred embodiment, the extruder is a shear-induced extruder.

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The temperature is preferably applied by extruding the precursor polyethylene composition (PPC) at an extruding temperature in the above described range.

5 The specific energy is preferably applied by extruding the precursor polyethylene composition (PPC) at a certain screw speed of the one or two screws of the extruder.

The further compounding conditions preferably are as follows:

10 The mixer speed is preferably in the range of from 200 to 750 rpm, more preferably in the range of from 300 to 500 rpm such as suitably in the range from 350 to 400 rpm.

The gear pump suction pressure is preferably in the range of from 1.0 bar to 10 bar, more preferably in the range of from 1.5 bar to 5.0 bar, such as suitably in the range of from 2.0 bar to 3.0 bar.

15 The gate opening is preferably in the range of from 10% to 50%, more preferably in the range of from 15% to 40%, such as suitably in the range of from 20% to 30%.

20 The thermoplastic polyethylene composition (TPC) is preferably pelletized as known in the art.

It has been found that by reacting the ethylene-hexene copolymer (PE) and the modifier (M) according to the process of the invention as described above and below that the resulting thermoplastic polyethylene composition (TPC) has a higher hydrostatic pressure resistance and/or a higher stress crack resistance.

25 In one embodiment, the hydrostatic pressure resistance is increased and the slow crack growth resistance is at least maintained, more preferably both the hydrostatic pressure resistance and the slow crack growth resistance are increased.

30 The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm at a temperature of 80 °C and a

hoop stress of 5.6 MPa, that is at least 500%, more preferably by 800%, most preferably by 1000% higher than for an equivalent pipe formed from a polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M).

- 5 The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm at a temperature of 80 °C and a hoop stress of 6.43 MPa, that is at least 500%, more preferably 800%, most preferably 1000%, higher than for an equivalent pipe formed from a polyethylene composition based on  
10 the ethylene-hexene copolymer (PE) without the modifier (M).

- The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm at a temperature of 80 °C and a  
15 hoop stress of 5.98 MPa, that is at least 100%, more preferably 200%, most preferably 250%, higher than for an equivalent pipe formed from a polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M).

- The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure  
20 resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm at a temperature of 20 °C and a hoop stress of 12.6 MPa, that is at least 100%, more preferably by 150%, most preferably by 200%, higher than for an equivalent pipe formed from a polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M).

- 25 The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm at a temperature of 20 °C and a hoop stress of 12.4 MPa, that is at least 100%, more preferably 150%, most preferably  
30 200%, higher than for an equivalent pipe formed from a polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M).

The thermoplastic polyethylene composition (TPC) preferably has a slow crack growth resistance (NPT), determined according to ISO 13479 on a pipe specimen having an outer diameter of 110 mm, an average wall thickness of 10 mm, notch depth of 2 mm, and notch length of 150 mm, at a temperature of 80 °C and a pressure of 4.6 MPa, that is at least 20%,  
5 more preferably 40%, most preferably 60%, higher than for an equivalent pipe formed from a polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M).

Whilst the primary finding of the present invention relates to the improved pipe properties of  
10 the thermoplastic polyethylene composition (TPC), further improvements are also observed in the rheological properties.

It has been found that by reacting the ethylene-hexene copolymer (PE) and the modifier (M) according to the process of the invention as described above and below that the resulting  
15 thermoplastic polyethylene composition (TPC) has a higher viscosity at a constant shear stress of 747 Pa,  $\eta_{747}$ , a lower melt flow rate  $MFR_5$ , a broader flow rate ratio  $FRR_{21/5}$ , a broader shear thinning index  $SHI_{5/300}$ , a broader shear thinning index  $SHI_{2.7/210}$ , and a broader shear thinning index  $SHI_{5/200}$ , compared to a thermoplastic polyethylene composition which includes the same ethylene-hexene copolymer (PE) and the same optional additives and  
20 carbon black but does not include the modifier (M) and is compounded using comparable compounding conditions.

The thermoplastic polyethylene composition (TPC) preferably has a viscosity at a constant shear stress of 747 Pa,  $\eta_{747}$ , which in the range of 10 to 500% higher, more preferably 20 to  
25 200% higher, still more preferably 30 to 150% higher and most preferably in the range of 40 to 100% higher than the viscosity at a constant shear stress of 747 Pa of the polyethylene composition based on ethylene-hexene copolymer (PE) without the modifier (M),  $\eta_{747}$  (PE).

The melt flow rate  $MFR_5$  of the thermoplastic polyethylene composition (TPC) is preferably  
30 in the range of 60 to 95 %, more preferably 70 to 92%, most preferably in the range of 80 to 90%, of the melt flow rate of the polyethylene composition based on ethylene-hexene copolymer (PE) without the modifier (M),  $MFR_5$  (PE).

The flow rate ratio  $FRR_{21/5}$  of the thermoplastic polyethylene composition (TPC) is preferably in the range of 1.0 to 30.0% higher, more preferably 1.5 to 20.0% higher, still more preferably 2.0 to 15.0% higher and most preferably in the range of 5.0 to 10.0% higher  
5 than the flow rate ratio of the polyethylene composition based on the ethylene-hexene copolymer (PE) without the modifier (M),  $FRR_{21/5}$  (PE).

The shear thinning index  $SHI_{5/200}$  of the thermoplastic polyethylene composition (TPC) is preferably in the range of 2.0 to 80.0% higher, more preferably 3.5 to 65.0% higher, still  
10 more preferably 5.0 to 40.0% higher and most preferably in the range of 7.5 to 25.0% higher than the shear thinning index of the polyethylene composition based on ethylene-hexene copolymer (PE) without the modifier (M),  $SHI_{5/200}$  (PE).

All fallback positions and preferably embodiments for the precursor polyethylene  
15 composition (PPC) of the first aspect and the thermoplastic polyethylene composition (TPC) of the third aspect apply mutatis mutandis to the precursor polyethylene composition (PPC) and the thermoplastic polyethylene composition (TPC) of the process of the second aspect.

#### **Thermoplastic polyethylene composition (TPC)**

20

In a third aspect, the present invention is directed to a thermoplastic polyethylene composition (TPC) obtainable, more preferably obtained, by the process of the second aspect.

25 The thermoplastic polyethylene composition (TPC) preferably has a density, determined according to ISO 1183-1:2004, in the range from 950 to 975 kg/m<sup>3</sup>, more preferably in the range from 954 to 970 kg/m<sup>3</sup>, most preferably in the range from 958 to 965 kg/m<sup>3</sup>.

30 The thermoplastic polyethylene composition (TPC) preferably has a 1-hexene content, determined according to quantitative <sup>13</sup>C-NMR spectroscopy, in the range from 0.8 to 2.0 wt.-%, more preferably in the range from 0.8 to 1.8 wt.-%, most preferably in the range from 0.8 to 1.5 wt.-%.

- 25 -

The thermoplastic polyethylene composition (TPC) preferably has a melt flow rate (MFR<sub>5</sub>), determined according to ISO 1133 at 190 °C and 5.0 kg, in the range from 0.10 to 1.00 g/10 min, more preferably in the range from 0.12 to 0.50 g/10 min, most preferably in the range from 0.15 to 0.30 g/10 min.

The thermoplastic polyethylene composition (TPC) preferably has a melt flow rate (MFR<sub>21</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg, in the range from 3.0 to 30.0 g/10 min, more preferably in the range from 4.0 to 20.0 g/10 min, most preferably in the range from 5.0 to 15.0 g/10 min.

The thermoplastic polyethylene composition (TPC) preferably has a flow rate ratio (FRR<sub>21/5</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg / 5 kg, in the range from 25 to 45, more preferably in the range from 28 to 40, most preferably in the range from 31 to 38.

The thermoplastic polyethylene composition (TPC) preferably has a viscosity at a shear stress of 747 Pa ( $\eta_{747}$ ), determined according to the measurement method given in the determination methods, in the range from 500 to 1000 kPa.s, more preferably in the range from 600 to 1000 kPa.s, most preferably in the range from 700 to 1000 kPa.s.

The thermoplastic polyethylene composition (TPC) preferably has a zero shear viscosity, determined according to the measurement method given in the determination methods, in the range from 2000 to 5000 kPa.s, more preferably in the range from 2300 to 4500 kPa.s, most preferably in the range from 2500 to 4000 kPa.s.

The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index (SHI<sub>5/200</sub>), determined according to the measurement method given in the determination methods, in the range from 50 to 70, more preferably in the range from 52 to 65, most preferably in the range from 54 to 60.

The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index (SHI<sub>0/50</sub>), determined according to the measurement method given in the determination

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methods, in the range from 50 to 90, more preferably in the range from 55 to 85, most preferably in the range from 60 to 80.

5 The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index ( $SHI_{0/100}$ ), determined according to the measurement method given in the determination methods, in the range from 100 to 220, more preferably in the range from 130 to 210, most preferably in the range from 150 to 200.

10 The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index ( $SHI_{1/100}$ ), determined according to the measurement method given in the determination methods, in the range from 30 to 80, more preferably in the range from 35 to 70, most preferably in the range from 40 to 60.

15 The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index ( $SHI_{2.7/210}$ ), determined according to the measurement method given in the determination methods, in the range from 70 to 150, more preferably in the range from 80 to 130, most preferably in the range from 90 to 110.

20 The thermoplastic polyethylene composition (TPC) preferably has a shear thinning index ( $SHI_{5/300}$ ), determined according to the measurement method given in the determination methods, in the range from 130 to 190, more preferably in the range from 140 to 180, most preferably in the range from 150 to 170.

25 The thermoplastic polyethylene composition (TPC) preferably has a crossover frequency, determined according to the measurement method given in the determination methods, in the range from 0.40 to 0.69 rad/s, more preferably in the range from 0.50 to 0.68 rad/s, most preferably in the range from 0.55 to 0.67 rad/s.

30 The thermoplastic polyethylene composition (TPC) preferably has a crossover modulus ( $G'c$ ), determined according to the measurement method given in the determination methods, in the range from 24.0 to 29.0 kPa, more preferably in the range from 25.0 to 28.5 kPa, most preferably in the range from 26.0 to 28.0 kPa.

The thermoplastic polyethylene composition (TPC) preferably has a rheological polydispersity index (PI), determined according to the measurement method given in the determination methods, in the range from 3.60 to 3.90, more preferably in the range from 3.63 to 3.80, most preferably in the range from 3.65 to 3.70.

The thermoplastic polyethylene composition (TPC) preferably has a Charpy Notched Impact Strength at -20 °C, determined according to ISO 179/1eA, in the range from 10.0 to 25.0 kJ/m<sup>2</sup>, more preferably in the range from 12.0 to 22.0 kJ/m<sup>2</sup>, most preferably in the range from 14.0 to 20.0 kJ/m<sup>2</sup>.

The thermoplastic polyethylene composition (TPC) preferably has a Charpy Notched Impact Strength at 23 °C, determined according to ISO 179-1:2010, in the range from 20 to 100 kJ/m<sup>2</sup>, more preferably in the range from 25 to 70 kJ/m<sup>2</sup>, most preferably in the range from 30 to 50 kJ/m<sup>2</sup>.

The thermoplastic polyethylene composition (TPC) preferably has a tensile modulus, determined according to ISO 527-2:2012, in the range from 800 to 1600 MPa, more preferably in the range from 900 to 1400 MPa, most preferably in the range from 1000 to 1200 MPa.

The thermoplastic polyethylene composition (TPC) preferably has a strain hardening modulus, determined according to the measurement method given in the determination methods, in the range from 50 to 90 MPa, more preferably in the range from 55 to 80 MPa, most preferably in the range from 60 to 75 MPa.

The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 80 °C and a hoop stress of 5.6 MPa, of at least 5000 hours, more preferably at least 6000 hours, most preferably at least 7000 hours.

The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 80 °C and a hoop stress of 6.43 MPa, of at least 100 hours, more preferably at least 300 hours, most preferably at least 500 hours.

The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 80 °C and a hoop stress of 5.98 MPa, of at least 5000 hours, more preferably at least 6000 hours, most preferably at least 7000 hours.

The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 20 °C and a hoop stress of 12.6 MPa, of at least 550 hours, more preferably at least 650 hours, most preferably at least 750 hours.

The thermoplastic polyethylene composition (TPC) preferably has a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 20 °C and a hoop stress of 12.4 MPa, of at least 1000 hours, more preferably at least 1300 hours, most preferably at least 1500 hours.

The thermoplastic polyethylene composition (TPC) preferably has a slow crack growth resistance (NPT), determined according to ISO 13479 on a pipe specimen having an outer diameter of 110 mm, an average wall thickness of 10 mm, notch depth of 2 mm, and notch length of 150 mm, at a temperature of 80 °C and a pressure of 4.6 MPa, of at least 2000 hours, more preferably of at least 2300 hours, most preferably of at least 2500 hours.

All fallback positions and preferable embodiments of the process for producing the thermoplastic polyethylene composition (TPC) of the second aspect apply mutatis mutandis

to the thermoplastic polyethylene composition (TPC) obtainable by said process of the third aspect.

#### Articles

5

In a fourth aspect, the present invention is directed to an article comprising the thermoplastic polyethylene composition (TPC) of the third aspect, which is selected from a pipe, film or blow moulded article.

10 Most preferably, the article is a pipe.

Preferably, the article is a pipe having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 5.6 MPa, of at least 5000 hours, more preferably at least 6000 hours, most preferably at least 7000 hours.

15

Preferably, the article is a pipe having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 6.43 MPa, of at least 100 hours, more preferably at least 300 hours, most preferably at least 500 hours.

20 Preferably, the article is a pipe having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 5.98 MPa, of at least 5000 hours, more preferably at least 6000 hours, most preferably at least 7000 hours.

25 Preferably, the article is a pipe having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 20 °C and a hoop stress of 12.6 MPa, of at least 550 hours, more preferably at least 650 hours, most preferably at least 750 hours.

30 Preferably, the article is a pipe having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 20 °C and a hoop stress of 12.4 MPa, of at least 1000 hours, more preferably at least 1300 hours, most preferably at least 1500 hours.

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Preferably, the article is a pipe having a slow crack growth resistance (NPT), determined according to ISO 13479 at a temperature of 80 °C and a pressure of 4.6 MPa of at least 2000 hours, more preferably of at least 2300 hours, most preferably of at least 2500 hours.

- 5 All fallback positions and preferable embodiments of the thermoplastic polyethylene composition (TPC) of the third aspect apply mutatis mutandis to the article comprising said thermoplastic polyethylene composition (TPC) of the fourth aspect.

#### Use

10

In a final aspect, the present invention is directed to a use of a modifier having two or more ethylenically unsaturated groups in a precursor polyethylene composition that comprises a polyethylene and the modifier and is preferably free from radical initiators, for increasing the hydrostatic pressure resistance and/or slow crack growth resistance of a pipe formed from a thermoplastic polyethylene composition obtained by exposing the precursor polyethylene composition to a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

- 15 20 In one embodiment, the hydrostatic pressure resistance is increased and the slow crack growth resistance is at least maintained, more preferably both the hydrostatic pressure resistance and the slow crack growth resistance are increased.

- 25 In one embodiment increasing the hydrostatic pressure resistance means that the hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 5.6 MPa, has increased by at least 500%, more preferably by 800%, most preferably by 1000%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

- 30 In one embodiment increasing the hydrostatic pressure resistance means that the hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 6.43 MPa, has increased by at least 500%, more preferably by 800%,

most preferably by 1000%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

5 In one embodiment increasing the hydrostatic pressure resistance means that the hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 5.98 MPa, has increased by at least 100%, more preferably by 200%, most preferably by 250%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

10 In one embodiment increasing the hydrostatic pressure resistance means that the hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 20 °C and a hoop stress of 12.6 MPa, has increased by at least 100%, more preferably by 150%, most preferably by 200%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

15 In one embodiment increasing the hydrostatic pressure resistance means that the hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 20 °C and a hoop stress of 12.4 MPa, has increased by at least 100%, more preferably by 150%, most preferably by 200%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

20 In one embodiment improving the slow crack growth resistance means that the slow crack growth resistance (NPT), determined according to ISO 13479 at a temperature of 80 °C and a pressure of 4.6 MPa, has increased by at least 20%, more preferably by 40%, most preferably by 60%, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.

25 It is particularly preferred that the use of the modifier for increasing the hydrostatic pressure resistance and/or slow crack growth resistance of a pipe also improved the sagging resistance, wherein in one embodiment, improving the sagging resistance means that the  $\epsilon_{747}$  of the thermoplastic polyethylene composition, determined according to the measurement method given in the determination methods, is at least 10 to 500% higher,

more preferably 20 to 200% higher, still more preferably 30 to 150% higher and most preferably in the range of 40 to 100% higher than an equivalent polyethylene composition based on the polyethylene without the modifier.

- 5 In the broadest sense, the polyethylene of the final aspect may be any polyethylene. More preferably, it is an ethylene/C<sub>3-8</sub> alpha olefin copolymer, yet more preferably an ethylene-hexene copolymer. Most preferably, the polyethylene is the ethylene-hexene copolymer (PE) of the first aspect.

- 10 It is also preferred that the modifier of the final aspect is the modifier (M) of the first aspect.

It is preferred that the precursor polyethylene composition is the precursor polyethylene composition (PPC) of the first aspect.

- 15 It is also preferred that the thermoplastic polyethylene composition is the thermoplastic polyolefin composition (TPC) of the third aspect.

It is preferred that the thermoplastic polyethylene composition is obtained by exposing the precursor composition to a process according to the second aspect.

20

All fallback positions and preferably embodiments of the first, second, and third aspects apply mutatis mutandis to the use of the final aspect.

## EXAMPLES

### 1. Determination Methods

The following definitions of terms and determination methods apply for the above general  
5 description of the invention as well as to the below examples unless otherwise defined.

#### Melt flow rate

The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min.  
The MFR is an indication of the flowability, and hence the processability, of the polymer.  
10 The higher the melt flow rate, the lower the viscosity of the polymer. The MFR<sub>5</sub> of  
polyethylene is measured at a temperature of 190 °C and a load of 5 kg, the MFR<sub>2</sub> of  
polyethylene at a temperature of 190 °C and a load of 2.16 kg and the MFR<sub>21</sub> of polyethylene  
is measured at a temperature of 190 °C and a load of 21.6 kg. The quantity FRR (flow rate  
ratio) denotes the ratio of flow rates at different loads. Thus, FRR<sub>21/5</sub> denotes the value of  
15 MFR<sub>21</sub>/MFR<sub>5</sub>.

#### Density

Density of the polymer was measured according to ISO 1183-1:2004 Method A on  
compression moulded specimen prepared according to EN ISO 1872-2 (Feb 2007) and is  
20 given in kg/m<sup>3</sup>.

#### DSC analysis, melting temperature (T<sub>m</sub>) and heat of fusion (H<sub>f</sub>), crystallization temperature (T<sub>c</sub>) and melt enthalpy (H<sub>m</sub>)

Measured with a TA Instrument Q2000 differential scanning calorimetry (DSC) on 5 to 7 mg  
25 samples. DSC is run according to ISO 11357 / part 3 /method C2 in a heat / cool / heat cycle  
with a scan rate of 10 °C/min in the temperature range of 0 to +200 °C. The crystallization  
temperature (T<sub>c</sub>) is determined from the cooling step, while melting temperature (T<sub>m</sub>) and  
melting enthalpy (ΔH<sub>m</sub>) are determined from the second heating step. The crystallinity is  
calculated from the melting enthalpy by assuming an ΔH<sub>m</sub>-value of 290 J/g for a fully  
30 crystalline polyethylene (see L. Mandelkern, R. G. Alamo, In Physical properties of  
polymers handbook, 2nd ed., Mark, J.E., Eds. Springer: New York, 2007)

### 1-Hexene content

Quantitative nuclear-magnetic resonance (NMR) spectroscopy was used to quantify the comonomer content of the polymers.

Quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra recorded in the molten-state using a Bruker Avance III  
5 500 NMR spectrometer operating at 500.13 and 125.76 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  respectively. All spectra were recorded using a  $^{13}\text{C}$  optimised 7 mm magic-angle spinning (MAS) probehead at 150°C using nitrogen gas for all pneumatics. Approximately 200 mg of material was packed into a 7 mm outer diameter zirconia MAS rotor and spun at 4 kHz. This setup was chosen primarily for the high sensitivity needed for rapid identification and accurate  
10 quantification (Klimke, K., Parkinson, M., Piel, C., Kaminsky, W., Spiess, H.W., Wilhelm, M., Macromol. Chem. Phys. 2006;207:382., Parkinson, M., Klimke, K., Spiess, H.W., Wilhelm, M., Macromol. Chem. Phys. 2007;208:2128., Castignolles, P., Graf, R., Parkinson, M., Wilhelm, M., Gaborieau, M., Polymer 50 (2009) 2373). Standard single-pulse excitation was employed utilising the transient NOE at short recycle delays of 3s (Pollard, M., Klimke,  
15 K., Graf, R., Spiess, H.W., Wilhelm, M., Sperber, O., Piel, C., Kaminsky, W., Macromolecules 2004;37:813., Klimke, K., Parkinson, M., Piel, C., Kaminsky, W., Spiess, H.W., Wilhelm, M., Macromol. Chem. Phys. 2006;207:382.) and the RS-HEPT decoupling scheme (Filip, X., Tripon, C., Filip, C., J. Mag. Resn. 2005, 176, 239, Griffin, J.M., Tripon, C., Samoson, A., Filip, C., and Brown, S.P., Mag. Res. in Chem. 2007 45, S1, S198). A total  
20 of 16348 (16k) transients were acquired per spectrum. This setup was chosen due its high sensitivity towards sometimes low comonomer contents.

Quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were processed, integrated and quantitative properties determined using custom spectral analysis automation programs. All chemical shifts are internally referenced to the bulk methylene signal ( $\delta^+$ ) at 30.00 ppm (J. Randall, Macromol.  
25 Sci., Rev. Macromol. Chem. Phys. 1989, C29, 201).

Characteristic signals corresponding to the incorporation of 1-hexene were observed (J. Randall, Macromol. Sci., Rev. Macromol. Chem. Phys. 1989, C29, 201.) and all contents calculated with respect to all other monomers present in the polymer.

Characteristic signals resulting from isolated 1-hexene incorporation i.e. EEHEE comonomer  
30 sequences, were observed. Isolated 1-hexene incorporation was quantified using the integral of the signal at 38.2 ppm assigned to the  $^*\text{B4}$  sites, accounting for the number of reporting sites per comonomer:

$$H = I_{*B4}$$

When characteristic signals resulting from consecutive 1-hexene incorporation, i.e. EHHE comonomer sequences were observed, such consecutive 1-hexene incorporation was quantified using the integral of the signal at 40.4 ppm assigned to the  $\alpha\alpha B4B4$  sites

5 accounting for the number of reporting sites per comonomer:

$$HH = 2 * I_{\alpha\alpha B4B4}$$

When characteristic signals resulting from non-consecutive 1-hexene incorporation, i.e. EHEHE comonomer sequences were observed, such non-consecutive 1-hexene incorporation was quantified using the integral of the signal at 24.6 ppm assigned to the  $\beta\beta B4B4$  sites

10 accounting for the number of reporting sites per comonomer:

$$HEH = 2 * I_{\beta\beta B4B4}$$

Due to the overlap of the signals from the  $*B4$  and  $*\beta B4B4$  sites from isolated (EEHEE) and non-consecutively incorporated (EHEHE) 1-hexene respectively the total amount of isolated 1-hexene incorporation is corrected based on the amount of non-consecutive 1-hexene

15 present:

$$H = I_{*B4} - 2 * I_{\beta\beta B4B4}$$

With no other signals indicative of other comonomer sequences, i.e. 1-hexene chain initiation, observed the total 1-hexene comonomer content was calculated based solely on the amount of isolated (EEHEE), consecutive (EHHE) and non-consecutive (EHEHE) 1-hexene

20 comonomer containing sequences:

$$H_{total} = H + HH + HEH$$

Characteristic signals resulting from saturated end-groups were observed. The content of such saturated end-groups was quantified using the average of the integral of the signals at 22.8 and 32.2 ppm assigned to the 2s and 3s sites respectively:

25 
$$S = (1/2) * (I_{2S} + I_{3S})$$

The relative content of ethylene was quantified using the integral of the bulk methylene ( $\delta^+$ ) signals at 30.00 ppm:

$$E = (1/2) * I_{\delta^+}$$

30 The total ethylene content was calculated based the bulk methylene signals and accounting for ethylene units present in other observed comonomer sequences or end-groups:

$$E_{total} = E + (2/2) * H + (1/4) * HH + (3/4) * HEH + (3/2) * S$$

The total mole fraction of 1-hexene in the polymer was then calculated as:

- 36 -

$$fH = H_{\text{total}} / (E_{\text{total}} + H_{\text{total}})$$

The total comonomer incorporation of 1-hexene in mole percent was calculated from the mole fraction in the usual manner:

$$H [\text{mol-}\%] = 100 * fH$$

- 5 The total comonomer incorporation of 1-hexene in weight percent was calculated from the mole fraction in the standard manner:

$$H [\text{wt-}\%] = 100 * (fH * 84.16) / ((fH * 84.16) + ((1-fH) * 28.05))$$

The comonomer incorporation of 1-hexene in mole percent in high Mw fraction was calculated from the total comonomer incorporation in the usual manner:

- 10  $H \text{ in HMW } [\text{mol-}\%] = 100 \% * H [\text{mol-}\%] / \text{Split of HMW fraction } \%$

### Dynamic Rheology

- The characterization of polymer melts by dynamic shear measurements complies with ISO standards 6721-1 and 6721-10. The measurements were performed on an Anton Paar MCR301 stress controlled rotational rheometer, equipped with a 25 mm parallel plate geometry. Measurements were undertaken on compression moulded plates using nitrogen atmosphere and setting a strain within the linear viscoelastic regime. The oscillatory shear tests were done at 190°C applying a frequency range between 0.01 and 600 rad/s and setting a gap of 1.2 mm. In a dynamic shear experiment the probe is subjected to a homogeneous deformation at a sinusoidal varying shear strain or shear stress (strain and stress controlled mode, respectively). On a controlled strain experiment, the probe is subjected to a sinusoidal strain that can be expressed by

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (1)$$

- If the applied strain is within the linear viscoelastic regime, the resulting sinusoidal stress response can be given by

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (2)$$

where  $\sigma_0$ , and  $\gamma_0$  are the stress and strain amplitudes, respectively;  $\omega$  is the angular frequency;  $\delta$  is the phase shift (loss angle between applied strain and stress response);  $t$  is the time.

- Dynamic test results are typically expressed by means of several different rheological functions, namely the shear storage modulus,  $G'$ , the shear loss modulus,  $G''$ , the complex shear modulus,  $G^*$ , the complex shear viscosity,  $\eta^*$ , the dynamic shear viscosity,  $\eta'$ , the out-

of-phase component of the complex shear viscosity,  $\eta''$  and the loss tangent,  $\tan \eta$ , which can be expressed as follows:

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \text{ [Pa]} \quad (3)$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \text{ [Pa]} \quad (4)$$

$$5 \quad G^* = G' + iG'' \text{ [Pa]} \quad (5)$$

$$\eta^* = \eta' - i\eta'' \text{ [Pa}\cdot\text{s]} \quad (6)$$

$$\eta' = \frac{G''}{\omega} \text{ [Pa}\cdot\text{s]} \quad (7)$$

$$\eta'' = \frac{G'}{\omega} \text{ [Pa}\cdot\text{s]} \quad (8)$$

- 10 The determination of so-called Shear Thinning Index, which correlates with MWD and is independent of Mw, is done as described in equation 9.

$$\text{SHI}_{(x/y)} = \frac{\text{Eta}^* \text{ for } (G^* = x \text{ kPa})}{\text{Eta}^* \text{ for } (G^* = y \text{ kPa})} \quad (9)$$

- 15 For example, the  $\text{SHI}_{(2.7/210)}$  is defined by the value of the complex viscosity, in Pa s, determined for a value of  $G^*$  equal to 2.7 kPa, divided by the value of the complex viscosity, in Pa s, determined for a value of  $G^*$  equal to 210 kPa and the  $\text{SHI}_{(5/200)}$  is defined by the value of the complex viscosity, in Pa s, determined for a value of  $G^*$  equal to 5 kPa, divided by the value of the complex viscosity, in Pa s, determined for a value of  $G^*$  equal to  
20 200 kPa.

The values of storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex modulus ( $G^*$ ) and complex viscosity ( $\eta^*$ ) were obtained as a function of frequency ( $\omega$ ).

Thereby, e.g.  $\eta^*_{300\text{rad/s}}$  ( $\text{eta}^*_{300\text{rad/s}}$ ) is used as abbreviation for the complex viscosity at the frequency of 300 rad/s and  $\eta^*_{0.05\text{rad/s}}$  ( $\text{eta}^*_{0.05\text{rad/s}}$ ) is used as abbreviation for the complex

- 25 viscosity at the frequency of 0.05 rad/s.

The loss tangent  $\tan(\delta)$  is defined as the ratio of the loss modulus ( $G''$ ) and the storage modulus ( $G'$ ) at a given frequency. Thereby, e.g.  $\tan_{0.05}$  is used as abbreviation for the ratio of the loss modulus ( $G''$ ) and the storage modulus ( $G'$ ) at 0.05 rad/s and  $\tan_{300}$  is used as abbreviation for the ratio of the loss modulus ( $G''$ ) and the storage modulus ( $G'$ ) at 300 rad/s.

The elasticity balance  $\tan_{0.05}/\tan_{300}$  is defined as the ratio of the loss tangent  $\tan_{0.05}$  and the loss tangent  $\tan_{300}$ .

Besides the above mentioned rheological functions one can also determine other rheological parameters such as the so-called elasticity index  $EI(x)$ . The elasticity index  $Ei(x)$  is the value of the storage modulus,  $G'$  determined for a value of the loss modulus,  $G''$  of  $x$  kPa and can be described by equation 10.

$$EI(x) = G' \text{ for } (G'' = x \text{ kPa}) \text{ [Pa]} \quad (10)$$

For example, the  $EI(5\text{kPa})$  is defined by the value of the storage modulus  $G'$ , determined for a value of  $G''$  equal to 5 kPa.

The polydispersity index,  $PI$ , is defined by equation 11.

$$PI = \frac{10^5}{G'(\omega_{COP})}, \quad \omega_{COP} = \omega \text{ for } (G' = G'') \quad (11)$$

where  $\omega_{COP}$  is the cross-over angular frequency, determined as the angular frequency for which the storage modulus,  $G'$ , equals the loss modulus,  $G''$ .

Cross-over modulus is defined as the value of  $G'$  and  $G''$ , where  $G'$  equals  $G''$  at the cross-over angular frequency.

The values are determined by means of a single point interpolation procedure, as defined by Rheoplus software. In situations for which a given  $G^*$  value is not experimentally reached, the value is determined by means of an extrapolation, using the same procedure as before. In both cases (interpolation or extrapolation), the option from Rheoplus "*Interpolate y-values to x-values from parameter*" and the "*logarithmic interpolation type*" were applied.

References:

- [1] "Rheological characterization of polyethylene fractions", Heino, E.L., Lehtinen, A., Tanner J., Seppälä, J., Neste Oy, Porvoo, Finland, Theor. Appl. Rheol., Proc. Int. Congr. Rheol., 11th (1992), 1, 360-362.

[2] "The influence of molecular structure on some rheological properties of polyethylene", Heino, E.L., Borealis Polymers Oy, Porvoo, Finland, Annual Transactions of the Nordic Rheology Society, 1995.

[3] "Definition of terms relating to the non-ultimate mechanical properties of polymers", Pure & Appl. Chem., Vol. 70, No. 3, pp. 701-754, 1998.

#### **Viscosity eta747**

ISO 3219-1:2021 Part 1: Vocabulary and symbols for rotational and oscillatory rheometry

10 ISO 3219-2:2021 Part 2: General principles of rotational and oscillatory rheometry

The method which is used in connection with the present invention relates to the rheology of the polymer and is based on determination of the viscosity of the polymer at a very low, constant shear stress. A shear stress of 747 Pa has been selected for this method. The viscosity of the polymer at this shear stress is determined at a temperature of 190 °C and has been found  
15 to be inversely proportional to the gravity flow of the polymer, i.e. the greater the viscosity the lower the gravity flow. The determination of the viscosity at 747 Pa shear stress is made by using a rotational rheometer, which can be a constant stress rheometer as for example an Anton Paar MCR Series Rheometer. Rheometers and their function have been described in "Encyclopedia of Polymer Science and Engineering", 2nd Ed., Vol. 14, pp. 492-509. The  
20 measurements are performed under a constant shear stress between two 25 mm diameter plates (constant rotation direction). The gap between the plates is 1.2 mm. A 1.5 mm thick polymer sample is inserted between the plates.

The sample is temperature conditioned during 2 min before the measurement is started. The  
25 measurement is performed at 190°C. After temperature conditioning the measurement starts by applying the predetermined stress. The stress is maintained during 1800 s to let the system approach steady state conditions. After this time the measurement starts and the viscosity is calculated. The measurement principle is to apply a certain torque to the plate axis via a precision motor. This torque is then translated into a shear stress in the sample. This shear  
30 stress is kept constant. The rotational speed produced by the shear stress is recorded and used for the calculation of the viscosity of the sample.

### Molecular Weight

- Molecular weight averages ( $M_z$ ,  $M_w$  and  $M_n$ ), Molecular weight distribution (MWD) and its broadness, described by polydispersity index,  $PDI = M_w/M_n$  (wherein  $M_n$  is the number average molecular weight and  $M_w$  is the weight average molecular weight) were determined by Gel Permeation Chromatography (GPC) according to ISO 16014-4:2003 and ASTM D 6474-99 using the following formulas:

$$M_n = \frac{\sum_{i=1}^N A_i}{\sum (A_i/M_i)} \quad (1)$$

$$M_w = \frac{\sum_{i=1}^N (A_i \times M_i)}{\sum A_i} \quad (2)$$

$$M_z = \frac{\sum_{i=1}^N (A_i \times M_i^2)}{\sum (A_i/M_i)} \quad (3)$$

- For a constant elution volume interval  $\Delta V_i$ , where  $A_i$  and  $M_i$  are the chromatographic peak slice area and polyolefin molecular weight (MW). A GPC instrument, equipped with infrared (IR) detector was used with 3 x Olexis and 1x Olexis Guard columns and 1,2,4-trichlorobenzene (TCB, stabilized with 250 mg/L 2,6-Di tert butyl-4-methyl-phenol) as solvent at 160 °C and at a constant flow rate of 1 mL/min. 200 µL of sample solution were injected per analysis. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with at least 15 narrow MWD polystyrene (PS) standards in the range of 0,5 kg/mol to 11 500 kg/mol. Mark Houwink constants for PS, PE and PP used are as described per ASTM D 6474-99. All samples were prepared by dissolving 5.0 – 9.0 mg of polymer in 8 mL (at 160 °C) of stabilized TCB (same as mobile phase) for 2.5 hours for PP or 3 hours for PE at 160°C under continuous gentle shaking in the autosampler of the GPC instrument.

### Hydrostatic Pressure Testing

- HPT testing is conducted according to; ISO 1167-1:2006 Thermoplastics pipes, fittings and assemblies for the conveyance of fluids — Determination of the resistance to internal pressure — Part 1: General method. Tests are carried out at specified temperatures and stress levels. The pipes specimens used have an outer diameter of 32 mm and an average wall thickness of 3.2 mm.

### Slow crack growth (Notched Pipe Test)

- NPT testing is conducted according to ISO 13479:2009; Polyolefin pipes for the conveyance of fluids — Determination of resistance to crack propagation — Test method for slow crack

growth on notched pipes. The pipe specimens used have an outer diameter of 110 mm, an average wall thickness of 10mm, notch depth of 20% of the wall thickness i.e., 2mm, and notch length of 150mm. Tests are carried out at specified temperatures and stress levels, typically 80°C and 4.6MPa, respectively, for PE100 pipes

5

### **Charpy Impact Strength**

Charpy impact test is a single point test that measures a material's resistance to impact from a swinging pendulum and thus estimates the brittleness or toughness of notched or unnotched specimens under specified impact test conditions. Charpy impact is defined as the energy needed to initiate fracture and continue the fracture until the specimen is broken. The values (kJ/m<sup>2</sup>) obtained can be used for quality control or to differentiate general toughness. Test method used is ISO 179-1:2010 Plastics -- Determination of Charpy impact properties -- Part 1: Non-instrumented impact test. Injected moulded, extruded or machined or cast sheet are prepared and 5-10 specimens per sample are tested.

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### **Tensile Properties**

The method is used to investigate the tensile behaviour of the specimens and to determine the tensile modulus, tensile yield stress, tensile strength, elongation and other aspects of the tensile stress/strain relationship. The test specimen is extended along its major axis at constant speed until the specimen fractures or until the load or the elongation reaches some predetermined value. During this procedure, the load and strain sustained by the specimen is measured. Test method used is ISO 527-2:2012 Plastics -- Determination of tensile properties

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### **Strain Hardening Modulus**

Strain hardening modulus of the compounds was obtained from a tensile stress-strain curve above the natural draw ratio and represents the slope of the increase in the stress strain trend at very high strains (strain hardening regime). It was measured at 80°C and 20mm/min on pre-conditioned (120°C/hour) 300 µm thick specimens according to ISO 18488 method.

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**Specific Energy**

The specific energy is the total energy that is input by the motors for heating, melting, mixing and conveying the polymer during the extrusion process for each kilogram of material being processed. Specific energy values are measured/calculated by the software that operates typical compounders/extruders and are provided directly to the operator as such.

**2. Examples****2.1 Catalyst preparation**

For the polymerization of PE-1 and PE-2, Lynx 200 catalyst, commercially available from W.R. Grace (US), was employed.

For the polymerization of PE-3 and PE-4, a Ziegler-Natta catalyst prepared as described in example 1 of WO 99/51646 was employed.

**2.2 Polymerization of PE-1 to PE-4**

PE-1 to PE-4 were polymerized according to the following general procedure, according to the precise conditions given in Table 1.

Into a first loop reactor (i.e. prepolymerization reactor) having a volume of 50 dm<sup>3</sup> and operating at a temperature and pressure as indicated in Table 1, propane (C<sub>3</sub>, 50 kg/h), ethylene (C<sub>2</sub>, 2 kg/h), and hydrogen (H<sub>2</sub>, 5 g/h) were introduced for conducting a pre-polymerization step. In addition the Ziegler-Natta catalyst was introduced into the reactor together with triethylaluminium cocatalyst so that the ratio of aluminium to titanium was 15 mol/mol. For PE-1, PE-3, and PE-4, the catalyst feed rate into the first loop reactor (i.e. prepolymerization reactor) was 0.44 g/h, whilst the cocatalyst feed rate was 0.5 g/h into the prepolymerization reactor and 0.5 g/h into the second loop reactor (i.e. loop reactor in Table 1). For PE-2, for which the first reactor (i.e. prepolymerization reactor) was not employed, the catalyst was fed directed into the (sole) loop reactor at a feed rate of 0.44 g/h and the cocatalyst was introduced at a feed rate of 1.0 g/h.

The slurry was withdrawn intermittently from the prepolymerization reactor and directed to a second loop reactor having a volume of 500 dm<sup>3</sup> and operating at a temperature and pressure of as indicated in Table 1. Additionally, propane, ethylene and hydrogen were fed to the second loop reactor whereby the ethylene concentration and the hydrogen to ethylene ratio for example PE1 are listed in Table 1. The split, the density and melt index of the polymer fractions produced in the second loop reactor are listed in Table 1.

The slurry was withdrawn intermittently from the second loop reactor by using settling legs and directed to a gas phase reactor. The gas phase reactor was operated at a temperature and pressure as indicated in Table 1. Additional ethylene, 1-hexene comonomer (C<sub>6</sub>), and hydrogen were fed whereby the ethylene concentration, the 1-hexene to ethylene ratio and the hydrogen to ethylene ratio as well as the production split and the density of the polymers withdrawn from the gas phase reactor are listed in Table 1.

**Table 1** Polymerization conditions of **PE-1** to **PE-4**

|                                           | PE-1 | PE-2  | PE-3 | PE-4 |
|-------------------------------------------|------|-------|------|------|
| <b>Prepolymerizer:</b>                    |      |       |      |      |
| Temperature [°C]                          | 55   | -     | 70   | 70   |
| Pressure [bar]                            | 60.0 | -     | 57.4 | 57.3 |
| Split [wt.-%]                             | 1.6  | -     | 1.7  | 1.9  |
| <b>Loop:</b>                              |      |       |      |      |
| Temperature [°C]                          | 95   | 95    | 95   | 95   |
| Pressure [bar]                            | 60.0 | 57.8  | 55.8 | 55.9 |
| H <sub>2</sub> /C <sub>2</sub> [mol/kmol] | 900  | 578   | 500  | 630  |
| C <sub>2</sub> -concentration [mol-%]     | 3.0  | 3.1   | 5.3  | 7.3  |
| Split [wt.-%]                             | 49.4 | 52    | 45.3 | 48.1 |
| MFR <sub>2</sub> [g/10 min]               | 270  | 400   | 290  | 220  |
| Density [kg/m <sup>3</sup> ]              | 972  | 970.6 | 972  | 972  |
| <b>Gas phase:</b>                         |      |       |      |      |
| Temperature [°C]                          | 85   | 85    | 85   | 85   |
| Pressure [bar]                            | 20   | 20    | 20   | 20   |
| H <sub>2</sub> /C <sub>2</sub> [mol/kmol] | 8    | 35.9  | 2.8  | 5.0  |
| C <sub>6</sub> /C <sub>2</sub> [mol/kmol] | 42   | 38.2  | 68   | 31   |
| C <sub>2</sub> -concentration [mol-%]     | 15   | 12.5  | 6.2  | 5.6  |
| Split [wt.-%]                             | 49   | 48    | 53   | 50   |
| Density [kg/m <sup>3</sup> ]              | 948  | 950   | 949  | 950  |

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- The resultant polymer powder was purged with nitrogen (about 50 kg/h) for one hour, stabilized with commercial stabilizers (1100 ppm of Irganox 1010, 1100 ppm of Irgafos 168, and 1100 ppm of calcium stearate) and then extruded with a carbon black masterbatch (40 wt.-% carbon black in a polyethylene matrix; CBMB\_HDBM\_40 of ABU DHABI
- 5 POLYMERS CO. LTD (BOROUGE) for all compositions based on PE-1, PE-3, and PE-4, and HE0888A of Borealis AG for all compositions based on PE-2) to pellets in a Mixtron LCM 80 counter-rotating twin screw extruder (manufactured by KOBELCO, Kobe Steel, Japan), either with or without modifier (hexamethylene-1,6-dimaleimide, commercially available as Nexamite A48 from Nexam Chemical, Lund (SE)), according to the
- 10 compounding conditions given in Table 2.

- The properties of RE1 to RE4 are (within experimental error) the properties of PE-1 to PE-4 (with the exception of the density, which is higher in RE1 to RE4 due to the presence of carbon black). This holds for at least the Mw, Mn, Mz, Mw/Mn, MFR<sub>5</sub>, MFR<sub>21</sub>, FRR<sub>21/5</sub>,
- 15  $\eta_{747}$  and SHI<sub>5/200</sub>.

Table 2                      Compounding conditions for IE1, IE2, CE1 to CE3 and RE1 to RE4

|                        | RE1   | IE1    | RE2   | IE2   | RE3   | CE1   | CE2   | RE4   | CE3   |
|------------------------|-------|--------|-------|-------|-------|-------|-------|-------|-------|
| PE-1                   | 93.75 | 93.711 | -     | -     | -     | -     | -     | -     | -     |
| PE-2                   | -     | -      | 93.90 | 93.85 | -     | -     | -     | -     | -     |
| PE-3                   | -     | -      | -     | -     | 93.90 | 93.87 | 93.85 | -     | -     |
| PE-4                   | -     | -      | -     | -     | -     | -     | -     | 93.90 | 93.87 |
| Modifier               | -     | 390    | -     | 500   | -     | 300   | 500   | -     | 300   |
| CBMB                   | 5.90  | 5.90   | 5.75  | 5.75  | 5.75  | 5.75  | 5.75  | 5.75  | 5.75  |
| Additives              | 3500  | 3500   | 3500  | 3500  | 3500  | 3500  | 3500  | 3500  | 3500  |
| Compounding Conditions |       |        |       |       |       |       |       |       |       |
| Temperature            | 270   | 270    | 270   | 275   | 275   | 275   | 275   | 252   | 262   |
| Mixer speed            | 350   | 350    | 400   | 400   | 400   | 400   | 400   | 400   | 400   |
| Gear pump suc pressure | 2.9   | 3.2    | 2.7   | 2.7   | 2.7   | 2.7   | 2.7   | 2.7   | 2.7   |
| Gate opening           | 30.0  | 25.0   | 28.1  | 28.1  | 28.1  | 28.1  | 28.1  | 29.3  | 29.3  |
| Specific Energy        | 0.250 | 0.250  | 0.186 | 0.250 | 0.258 | 0.256 | 0.260 | 0.260 | 0.260 |

Table 3 Properties of IE1, IE2, CE1 to CE3 and RE1 to RE4

|                        | RE1   | IE1   | RE2   | IE2   | RE3   | CE1   | CE2   | RE4  | CE3   |
|------------------------|-------|-------|-------|-------|-------|-------|-------|------|-------|
| hexene-content         | 1.4   | 1.4   | 1.0   | 1.0   | 1.0   | 1.4   | 1.4   | 0.3  | 0.3   |
| MFR <sub>5</sub>       | 0.29  | 0.24  | 0.23  | 0.20  | 0.28  | 0.20  | 0.20  | 0.15 | 0.11  |
| MFR <sub>21</sub>      | 9.90  | 8.59  | 6.94  | 6.60  | 9.14  | 7.00  | 7.88  | 5.58 | 4.53  |
| FRR <sub>21/5</sub>    | 34.0  | 36.0  | 30.2  | 33.0  | 33.2  | 35.8  | 40.1  | 36   | 41.2  |
| Density                | 960.1 | 959.3 | 962.9 | 961.8 | 958.9 | 958.3 | 959.1 | n.m. | 961.1 |
| Eta <sub>747</sub>     | 455   | 767   | 632   | 922   | 642   | 1395  | 1409  | 957  | 1875  |
| Tm                     | 129.2 | 129.2 | n.m.  | n.m.  | 129.8 | 129.8 | 129.8 | n.m. | n.m.  |
| Tc                     | 118.8 | 118.7 | n.m.  | n.m.  | 119.3 | 119.4 | 119.4 | n.m. | n.m.  |
| Crossover frequency    | 0.91  | 0.65  | 0.74  | 0.60  | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| Crossover Modulus      | 29984 | 27246 | 29454 | 27081 | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| PI                     | 3.34  | 3.67  | 3.40  | 3.69  | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| Zero shear viscosity   | 1097  | 2782  | 1635  | 3648  | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| SHI <sub>0/50</sub>    | 27.9  | 61.9  | 35.3  | 76.2  | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| SHI <sub>0/100</sub>   | 68.5  | 155.1 | 86.6  | 188.5 | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| SHI <sub>1/100</sub>   | 26.1  | 45.7  | 30    | 51.7  | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| SHI <sub>2.7/210</sub> | 67.5  | 97.7  | 71.9  | 100.1 | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |
| SHI <sub>5/200</sub>   | 45.6  | 57.9  | 46.7  | 57.5  | 47.8  | 66.2  | 78.1  | n.m. | n.m.  |
| SHI <sub>5/300</sub>   | 128.5 | 165.1 | 129   | 156.6 | n.m.  | n.m.  | n.m.  | n.m. | n.m.  |

|                        | RE1       | IE1       | RE2       | IE2       | RE3       | CE1   | CE2    | RE4       | CE3   |
|------------------------|-----------|-----------|-----------|-----------|-----------|-------|--------|-----------|-------|
| Mw/Mn                  | 31.6      | 31.3      | 31.3      | n.m.      | 23.9      | n.m.  | n.m.   | 27.6      | n.m.  |
| Mn                     | 7945      | 7730      | 8320      | 7945      | 10250     | n.m.  | n.m.   | 9850      | n.m.  |
| Mw                     | 251,000   | 242,000   | 260,000   | 251,000   | 245,000   | n.m.  | n.m.   | 271,500   | n.m.  |
| Mz                     | 1,575,000 | 1,450,000 | 1,460,000 | 1,575,000 | 1,375,000 | n.m.  | n.m.   | 1,575,000 | n.m.  |
| Charpy NIS (+23 °C)    | 32.9      | 47.8      | 34.8      | 33.1      | 32.6      | 34.3  | 33.5   | 31.8      | n.m.  |
| Charpy NIS (-30 °C)    | 13.5      | 15.3      | 18.1      | 17.1      | 19.0      | 18.5  | 18.2   | 23.7      | n.m.  |
| SH Modulus             | 71.3      | 70.9      | 63.6      | 65.6      | 67.3      | 65.9  | 66.2   | 46.8      | 49.7  |
| Tens Modulus           | 1041      | 1010      | 1124      | 1115      | 1010.0    | 982.0 | 1020.0 | 1250      | n.m.  |
| Tens Stress @ Yield    | 24.7      | 24.1      | 26        | 26        | n.m.      | n.m.  | n.m.   | n.m.      | n.m.  |
| Tens Strain @ Yield    | 9.3       | 9.3       | 9.4       | 9.4       | n.m.      | n.m.  | n.m.   | n.m.      | n.m.  |
| Tens Strain @ Break    | 34.8      | 34.9      | 23.9      | 23.5      | 30.9      | 26.5  | 32.9   | 16.3      | n.m.  |
| Nominal Strain @ Break | 734.2     | 752.5     | 521.7     | 516.7     | 670.0     | 570.0 | 670.0  | 441       | n.m.  |
| HPT (20°C/12.6 MPa)    | 221       | 805       | 502       | 1432      | n.m.      | n.m.  | n.m.   | n.m.      | >9000 |
| HPT (20°C/12.4 MPa)    | 397       | 1916      | 1669      | 4713      | n.m.      | n.m.  | n.m.   | n.m.      | n.m.  |
| HPT (80°C/6.4 MPa)     | n.m.      | n.m.      | 27        | 555       | n.m.      | n.m.  | n.m.   | n.m.      | n.m.  |
| HPT (80°C/6.0 MPa)     | n.m.      | n.m.      | 2012      | 8036      | 446       | 521   | 528    | n.m.      | n.m.  |
| HPT (80°C/5.6 MPa)     | 718       | 9485      | n.m.      | n.m.      | n.m.      | n.m.  | n.m.   | n.m.      | b.f.  |
| NPT (80°C/4.6 MPa)     | 5685      | 8455      | >2500     | >2500     | n.m.      | n.m.  | n.m.   | n.m.      | 454   |

n.m. = not measured, b.f. = brittle failure

As can be seen from Table 3, the addition of a modifier (Nexamite A48) has the effect of notably improving both the hydrostatic pressure resistance (see HPT in Table 3) and the slow crack growth resistance (see NPT in Table 3) of the key ethylene-hexene copolymers PE-1 and PE-2. When PE-3 or PE-4 are used in place of PE-1 or PE-2, the effect of the modifier is much lower (see e.g. HPT 80°C/6.0 MPa for RE3, CE1 and CE2). Whilst CE3 has excellent low temperature hydrostatic pressure resistance, the high temperature hydrostatic pressure test results in brittle failure (which is an unacceptable failure mode), and the slow crack growth resistance is far too low, with the balance of HPT and NPT data far more favourable for IE1 and IE2.

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As would be clear to the person skilled in the art, this simultaneous improvement of HPT properties in combination with at least maintaining, usually improving, the NPT properties is particularly impressive, since these properties are generally understood to be inversely proportional for a given polymer, i.e. by improving HPT the NPT is usually worsened, and vice versa.

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In addition to these unexpected improvements in pipe properties, the addition of the modifier results in a number of further improvements that are apparent from Table 3. The improved  $\eta_{a747}$  values are key indicators that the pipes experience less sagging. The MFR decreases slightly, whilst the FRR and SHI both increase (reflecting the broadening of the molecular weight distribution). The modified rheological properties allow for improved processing.

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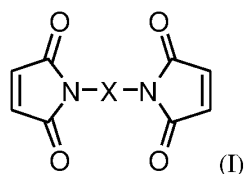
Furthermore, all of these effects are achieved whilst at least maintaining the mechanical properties (e.g. Charpy NIS, strain hardening, and tensile properties) of the ethylene-hexene copolymer base resins.

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Finally, it was also noticed that the pipes prepared from IE1 and IE2 had improved surface appearance (without lumpiness or high roughness), in contrast to known polyethylene pipes containing cross-linking additives.

## CLAIMS

1. A precursor polyethylene composition (PPC), comprising:
  - a) an ethylene-hexene copolymer (PE) having:
    - i) a melt flow rate (MFR<sub>5</sub>), determined according to ISO 1133 at 190 °C and 5.0 kg, in the range from 0.10 to 1.00 g/10 min;
    - ii) a 1-hexene content, determined according to quantitative <sup>13</sup>C-NMR spectroscopy, in the range from 0.8 to 2.0 wt.-%; and
    - iii) a molecular weight distribution (Mw/Mn), determined by gel permeation chromatography (GPC), in the range from 28.5 to 40.0, and
  - b) a modifier (M) having two or more ethylenically unsaturated groups, wherein the ethylene-hexene copolymer (PE) and the modifier (M) are reactive to form a thermoplastic polyethylene composition at a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg.
2. The precursor polyethylene composition (PPC) according to claim 1, wherein the precursor polyethylene composition (PPC) contains less than 2.0 wt.-% of radical initiators, more preferably less than 1.0 wt.-% of radical initiators, most preferably is free from radical initiators.
3. The precursor polyethylene composition (PPC) according to claim 1 or claim 2, wherein the modifier (M) has a structure according to formula (I):



wherein X is a linking group selected from the group consisting of phenylene and linear or branched C<sub>2</sub> to C<sub>10</sub> alkylene, more preferably X is selected from the group consisting of 1,4-phenylene and linear C<sub>4</sub> to C<sub>8</sub> alkylene, most preferably X is  $-(CH_2)_6-$ .

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4. The precursor polyethylene composition (PPC) according to any one of the preceding claims, wherein the ethylene-hexene copolymer (PE) has one or more, preferably all, of the following properties:
- 5           i) a melt flow rate (MFR<sub>21</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg, in the range from 3.0 to 30.0 g/10 min;
- ii) a flow rate ratio (FRR<sub>21/5</sub>), determined according to ISO 1133 at 190 °C and 21.6 kg / 5 kg, in the range from 25 to 40;
- 10          iii) a viscosity at a shear stress of 747 Pa ( $\eta_{747}$ ), determined according to the measurement method given in the determination methods, in the range from 400 to 700 kPa.s; and
- iv) a shear thinning index (SHI<sub>5/200</sub>), determined according to the measurement method given in the determination methods, in the range from 40 to 60.
5. The precursor polyethylene composition (PPC) according to any one of the preceding claims, wherein the ethylene-hexene copolymer (PE) has one or more, preferably all, of the following properties:
- 15           i) a number average molecular weight (Mn), determined according to ISO 16014-4, in the range from 6,000 to 9,000 g/mol;
- ii) a weight average molecular weight (Mw), determined according to ISO 16014-4, in the range from 200,000 to 300,000 g/mol; and
- 20          iii) a z-average molecular weight (Mz), determined according to ISO 16014-4, in the range from 1,200,000 to 1,900,000 g/mol.
6. The precursor polyethylene composition (PPC) according to any one of the preceding claims, wherein the ethylene-hexene copolymer (PE) comprises:
- 25           a) a low molecular weight fraction (PE1) being an ethylene homopolymer; and
- b) a high molecular weight fraction (PE2) being an ethylene-hexene copolymer, wherein the total amount of the low molecular weight fraction (PE1) and the high molecular weight fraction (PE2) is at least 90 wt.-%, and wherein the ratio of the low molecular weight fraction (PE1) and the high molecular weight fraction (PE2), [PE1]:[PE2], is preferably in the range from 50.5 : 49.5 to 60.0 : 40.0.
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7. The precursor polyethylene composition (PPC) according to any one of the preceding claims, wherein the modifier (M) is present in an amount in the range from 100 to 1500 ppm, more preferably in the range from 150 to 1200 ppm, yet more preferably in the range from 200 to 1000 ppm, even more preferably in the range from 250 to 800 ppm, most preferably in the range from 300 to 600 ppm, relative to the total weight of the precursor polyethylene composition (PPC).
8. The precursor polyethylene composition (PPC) according to any one of the preceding claims, further comprising carbon black (CB) in an amount in the range from 1.0 to 4.0 wt.-%, relative to the total weight of the precursor polyethylene composition (PPC).
9. A process for forming a thermoplastic polyethylene composition (TPC), comprising the steps of:
- providing a precursor polyethylene composition (PPC) according to any one of claims 1 to 8;
  - heating the precursor polyethylene composition (PPC) to a temperature of 180 to 300 °C; and
  - subjecting the precursor polyethylene composition (PPC) to a specific energy of equal to or more than 0.15 kWh/kg, thereby obtaining the thermoplastic polyethylene composition (TPC),
- wherein process steps b) and c) are preferably carried out simultaneously in a compounder, more preferably an extruder selected from a single-screw extruder and a twin-screw extruder,
- wherein the extruder is preferably operated at a mixer speed in the range of from 200 to 750 rpm.
10. A thermoplastic polyethylene composition (TPC) obtainable, more preferably obtained, by the process according to claim 9.
11. The thermoplastic polyethylene composition (TPC) according to claim 10, having a viscosity at a shear stress of 747 Pa ( $\eta_{747}$ ), determined according to the

measurement method given in the determination methods, in the range from 500 to 1000 kPa.s

- 5 12. The thermoplastic polyethylene composition (TPC) according to claim 10 or claim 11, having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 on a pipe specimen having an outer diameter of 32 mm and an average wall thickness of 3.2 mm, at a temperature of 80 °C and a hoop stress of 5.6 MPa, of at least 5000 hours and a slow crack growth resistance (NPT), determined according to ISO 13479 on a pipe specimen having an outer diameter of 110 mm, an average wall thickness of 10 mm, notch depth of 2 mm, and notch length of 150 mm, at a temperature of 80 °C and a pressure of 4.6 MPa of at least 2000 hours.
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13. An article comprising the thermoplastic polyethylene composition (TPC) according to any one of claims 10 to 12, which is preferably selected from a pipe, film or blow moulded article, most preferably a pipe.
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14. The article according to claim 13, being a pipe and having a hydrostatic pressure resistance (HPT), determined according to ISO 1167-1 at a temperature of 80 °C and a hoop stress of 5.6 MPa, of at least 5000 hours and a slow crack growth resistance (NPT), determined according to ISO 13479 at a temperature of 80 °C and a pressure of 4.6 MPa of at least 2000 hours.
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15. A use of a modifier having two or more ethylenically unsaturated groups in a precursor polyethylene composition that comprises a polyethylene and the modifier and is preferably free from radical initiators, for increasing the hydrostatic pressure resistance and/or slow crack growth resistance of a pipe formed from a thermoplastic polyethylene composition obtained by exposing the precursor polyethylene composition to a temperature in the range of from 180 to 300 °C and a specific energy equal to or greater than 0.15 kWh/kg, relative to an equivalent pipe formed from a polyethylene composition based on the polyethylene without the modifier.
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