

Polyethylene Composition for Container Articles

TECHNICAL FIELD

The present invention relates to a polyethylene composition, specifically to a multimodal high-density polyethylene (HDPE) composition exhibiting exceptional environmental stress crack resistance (ESCR) and processability for container articles.

BACKGROUND OF INVENTION

High-density polyethylene (HDPE) composition, which can be manufactured using various catalyst systems and polymerization processes, is well known for its high strength, chemical resistance, and versatility. HDPE composition, with its tailored molecular architecture, has gained significant attention due to its ability to balance mechanical properties and ease of processing.

In blow molding applications or container articles, HDPE compositions must exhibit a good balance between environmental stress crack resistance (ESCR), mechanical properties, and processability. Additionally, for blow-molded containers or container articles, the composition must address a variety of challenges such as sagging resistance during processing and swelling behavior that impacts the dimensional stability of such products. This is particularly important for hollowed medium- to large- blow mold articles, such as jerrycans and drums of various sizes and shapes, where stringent performance requirements are critical. With expected excellent ESCR performance, optimized rheological properties for superior processability with a well-balanced relaxation time. In these applications a combination of chemical resistance, mechanical durability, and efficient manufacturing are sought after but difficult to achieve. The current invention also addresses the growing demand for advanced HDPE materials capable of meeting more stringent performance requirements in industrial packaging applications.

WO 2015/138674 A1 describes a polyethylene composition with a higher molecular weight component and a lower molecular weight component having high load melt index (HLMI) from about 15 to 100 g/10 min with improved stiffness and stress crack resistance (SCR) with good processability. WO 2021/021473 A1 discloses a polyethylene composition from chromium-based catalyst system with improved ESCR and rheological properties. WO 2024/056727 A1 highlights a polyethylene composition suitable for producing blow-molded hollow articles with focus on rheological properties and elasticity ratio (ER) to balance parison swell and mechanical properties. Also, US 2024/0093009 A1 teaches a polyethylene composition for blow-molded hollow articles with emphasize on the importance of rheological properties and ER to control swelling behaviour ensuring quality of the resulting blow-molded hollow articles.

US 2021/0024728 A1 introduces a polyethylene-based polymer composition with improved SCR from chromium-based catalyst with good processability, especially cycle time and surface quality for large blow-molded application. WO 2023/187477 A1 also discloses a polyethylene composition with a higher molecular weight component and a lower molecular weight component together with a low-density polyethylene in 1 to 20 percent weight of the total composition to increase die swell while still having good environmental stress cracking resistance and balancing other properties.

It can be acknowledged from the above-described references that various aspects of polyethylene compositions for blow-molded application have been explored. However, due to limitations found in prior arts, needs for developing a new composition remains. Especially, for further providing a comprehensive solution on improving environmental stress crack resistance (ESCR), mechanical properties, and processability.

It is therefore an object of the present invention to overcome drawbacks identified in the prior arts by providing a polyethylene composition with balanced improvement in processability. Particularly, the high-density polyethylene composition having high molecular weight while simultaneously maintaining excellent mechanical properties and superior environmental stress crack resistance (ESCR) for hollowed blow mold articles or container articles.

SUMMARY OF THE INVENTION

The present invention relates to a polyethylene composition comprising:

- a first ethylene homo- or co- polymer component (A) having a weight average molecular weight (Mw) of from 15,000 to 90,000 g/mol determined as set forth in the description; and
- a second ethylene homo- or co- polymer component (B) having a weight average molecular weight (Mw) of 300,000 to 1,100,000 g/mol determined as set forth in the description;

wherein the polyethylene composition has

- a density from 0.940 to 0.975 g/cm³ measured by ASTM D 1505;
- a MI₂₁ (melt flow index at load 21.6 kg and temperature of 190°C) from 1.0 to 70 g/10 min measured by ASTM D 1238.

The inventors have surprisingly found that the polyethylene composition having the first ethylene homo- or co- polymer component (A) and the second ethylene homo- or co- polymer component (B) with specific ratio of Mz/Mn and tan delta, such composition could provide exceptional environmental stress crack resistance (ESCR) and excellent rheology property for smoother processing, with better dimensional control under extrusion conditions, these combination of improvement ultimately improved mold filling and reduce cycle time for container article.

Preferred embodiments are set forth in the appended dependent claims. The present invention is described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

The present invention can be achieved by providing a polyethylene composition comprising

- a first ethylene homo- or co- polymer component (A) having a weight average molecular weight (Mw) of from 15,000 to 90,000 g/mol determined as set forth in the description; and
- a second ethylene homo- or co- polymer component (B) having a weight average molecular weight (Mw) of 300,000 to 1,100,000 g/mol determined as set forth in the description;

wherein the polyethylene composition has

- a density from 0.940 to 0.975 g/cm³ measured by ASTM D 1505;

- a MI_{21} (melt flow index at load 21.6 kg and temperature of 190°C) from 1.0 to 70 g/10 min measured by ASTM D 1238.

In detail, the present invention relates to a polyethylene composition. The polyethylene composition comprises a first ethylene homo- or copolymer component (A) and further comprises a second ethylene homo- or copolymer component (B).

The first ethylene homo- or copolymer component (A) has a weight average molecular weight from 15,000 to 90,000 g/mol. The second ethylene homo- or copolymer component (B) has a weight average molecular weight from 300,000 to 1,100,000 g/mol. Both the weight average molecular weight of component (A) and the weight average molecular weight of component (B) as described in the following and in the experimental part in detail.

The molecular weight distribution of the polyethylene composition is measured by high temperature Gel Permeation Chromatography (HT-GPC, so called GPC). The molecular weight distribution obtained this way, that is the GPC data (curve obtained by GPC under the conditions as set forth below in detail) is deconvoluted into the sum of two Gaussian distribution functions (wherein deconvolution is carried out as set forth below in detail).

The first ethylene homo- or co- polymer component (A) means the component corresponding to the Flory distribution function with the lower weight average molecular weight deconvoluted, wherein this component has a weight average molecular weight (M_w) from 15,000 to 90,000 g/mol, preferably from 15,000 to 80,000 g/mol, more preferably from 20,000 to 70,000 g/mol, most preferably from 20,000 to 60,000 g/mol.

The second ethylene homo- or co- polymer component (B) means the component, corresponding to the Flory distribution function with the higher weight average molecular weight deconvoluted, wherein this component has a weight average molecular weight (M_w) from 300,000 to 1,100,000 g/mol, preferably from 350,000 to 1,100,000 g/mol, more preferably from 400,000 to 950,000 g/mol, most preferably 450,000 to 900,000 g/mol.

wherein the M_w of each component is calculated from its respective fitted Gaussian distribution, especially as set forth below in detail.

In one aspect, the polyethylene composition of the present invention has a ratio between z-average molecular weight and number-average molecular weight (M_z/M_n) of from 80 to 220, preferably from 80 to 200, more preferably 90 to 190, even more preferably from 90 to 180, most preferably from 90 to 170.

In one aspect, the polyethylene composition of the present invention has a comonomer content 0.01 to 1.20 mol %, preferably 0.05 to 1.10 mol %, more preferably 0.1 to 1.10 mol %, most preferably 0.2 to 1.0 mol %, as determined using carbon-13 nuclear magnetic resonance (^{13}C -NMR). That is, in case that the component (A) and/or the component (B) is an ethylene copolymer the respective component comprises ethylene monomer units and copolymer monomer units and the comonomer content of the polyethylene composition is the amount comonomer unit in component (A) (if present) and the component (B) (if present) relative to the total amount of monomer units in both component (A) and component (B). The comonomer, that is the comonomer which may be comprised in component (A) and component (B) provided that the respective component is an ethylene

copolymer, may be a C₃ to C₁₂ alpha olefin, preferably may be independently selected from 1-butene or 1-hexene, or mixture thereof.

Preferably, the comonomer of the present polyethylene composition is selected from the group consisting of C₃ to C₁₂ α-olefin, preferably from 1-butene, 1-hexene, or 1-octene, more preferably from 1-butene or 1-hexene, or mixture thereof.

Preferably, a percentage of the total weight of component (A) is from 40 to 90 % by weight, preferably from 45 to 87 % by weight, even more preferably from 50 to 85 % by weight, and the total weight of component (B) from 10 to 60 % by weight, preferably from 13 to 55 % by weight, even more preferably from 15 to 50 % by weight.

The polyethylene composition according to the present invention may be produced in single stage or multistage process, preferably in a multistage process, where each ethylene homo- or copolymer forming the component (A) and the component (B) may be produced in a different polymerization step, that is, at different stages of the multistage process in any order.

A multistage process can, for example, be a slurry-gas-process, a gas-gas-process, solution-solution-process, a solution-solution-solution-process, slurry-gas-gas- process, particularly preferably a slurry-slurry-process, slurry-slurry-slurry-process. In this regard, the expressions "slurry", "gas", "solution" describe the type of reactor and the reaction condition in the respective stage. For example, a "slurry-gas-process" refers to a two-stage polymerization process that combines:

1. A slurry-phase reactor (for example a loop or stirred tank reactor), and
2. A gas-phase reactor (for example a fluidized-bed reactor).

Optionally the process according to the invention can comprise one or two additional slurry polymerization steps (stages).

The polyethylene composition according to the present invention may be obtained from single stage or multistage processes. Alternatively, one or more further polyethylene fractions and/or component may be added to the composition obtained from a single stage or a multistage process by physical blending to from the polyethylene composition. For example, component (A) may, in a first step, be prepared in a single stage process and component (B) is added to component (A) obtained this way by physical blending. In another example, component (A) and a first fraction of component (B) are prepared in a multistage process and a second fraction of component (B) is added by physical blending, wherein the first fraction of component (B) and the second fraction of component (B) form together component (B).

The polyethylene composition can be made of two or three ethylene homo- or copolymer fractions showing a bimodal molecular weight distribution in GPC when deconvoluted as described herein in detail.

The polyethylene composition can comprise two or more ethylene homo- or copolymer components, wherein of the components is component (A) and one of the components is component (B). Alternatively, the polyethylene composition may consist of component (A) and component (B). The polyethylene composition may consist of component (A) and component (B), wherein each of component (A) and component (B) may be formed of one

or more ethylene homo- or copolymer fractions. Respective fractions overlap with each other in a way that they show in GPC when deconvoluted as described herein one mode, that is, in, for example, a bimodal polyethylene composition, together one peak.

5 In one of embodiment, the polyethylene composition is a bimodal polyethylene composition comprising a first polyethylene homopolymer or copolymer having weight average molecular weight (Mw) of 15,000 to 90,000 g/mol; and a second polyethylene homopolymer or copolymer having an average molecular weight (Mw) of 300,000 to 1,100,000 g/mol g/mol, wherein the polyethylene composition has a density from 0.940 to 0.975 g/cm³ measured by ASTM D 1505; and a MI₂₁ (melt flow index at load 21.6 kg and temperature of 190°C) from 1.0 to 70 g/10 min measured by ASTM D 1238.

The bimodal polyethylene composition can be obtained from the two-stage polymerization process using a first reactor and a second reactor in series, preferably a slurry-slurry process. Preferably, the bimodal polyethylene composition is obtained from the two-stage polymerization process as follows.

15 The first reactor

(a) In the first reactor, ethylene and optionally C₃ to C₁₂ α-olefin comonomer, such as 1-butene is polymerized in an inert hydrocarbon medium in the presence of hydrogen, in the presence of a Ziegler-Natta catalyst, such as the Ziegler-Natta catalyst as described in Hungarian patent application number 0800771R in the examples such as in example 1, to
20 obtain a low molecular weight polyethylene homopolymer or copolymer having a weight average molecular weight of 15,000 to 90,000 g/mol.

The second reactor

(b) The obtained polyethylene homopolymer or copolymer from the first reactor is transferred to a second reactor.

25 (c) In the second reactor, ethylene and optionally C₃ to C₁₂ α-olefin comonomer is polymerized in an inert hydrocarbon medium in the presence of hydrogen, to obtain a low molecular weight polyethylene homopolymer or copolymer having a weight average molecular weight of 300,000 to 1,100,000 g/mol.

The weight ratio of the polyethylene homopolymer or copolymer obtained from the first reactor to the polyethylene homopolymer or copolymer obtained from the second reactor
30 may be from 40:60 to 90:10.

Preferably, the Ziegler-Natta catalyst is prepared in accordance with the method described in Hungarian patent application number 0800771, as demonstrated in the examples, especially example 1, and with triethylaluminum as the co-catalyst.

35 The bimodal polyethylene may have a total amount of comonomer, the comonomer preferably being selected from 1-butene or 1-hexene, from 0.01 to 1.2 % by mol (mol%), with respect to the total amount of monomer in the polyethylene composition.

In one aspect, the polyethylene composition of the present invention has the percentage of the total weight of component (A) from 40 to 90 % by weight, preferably from 45 to 87 % by
40 weight, even more preferably from 50 to 85 % by weight, and the total weight of component

(B) from 10 to 60 % by weight, preferably from 13 to 55 % by weight, even more preferably from 15 to 50 % by weight.

In another aspect, the polyethylene composition of the present invention has the first ethylene homo- or co- polymer component (A) with weight average molecular weight (Mw) as deconvoluted from GPC curve from 15,000 to 90,000 g/mol, preferably from 15,000 to 80,000 g/mol, more preferably from 20,000 to 70,000 g/mol, most preferably from 20,000 to 60,000 g/mol. In this aspect, the polyethylene composition of the present invention has the second ethylene homo- or co- polymer component (B) with weight average molecular weight (Mw) as deconvoluted from GPC curve from 300,000 to 1,100,000 g/mol, preferably from 350,000 to 1,100,000 g/mol, more preferably from 400,000 to 950,000 g/mol, most preferably 450,000 to 900,000 g/mol.

In one aspect, the polyethylene composition of the present invention has an Environmental Stress Crack Resistance (ESCR) of more than or equal to 1,000 hours, preferably more than or equal to 2,000 hours, more preferably more than or equal to 3,000 hours, most preferably more than or equal to 4,000 hours, as measured according to ASTM D1693 (10% Igepal, F50, Condition B).

In one aspect, the polyethylene composition of the present invention has a SHT between 25 to 50 MPa, preferably between 28 to 45 MPa, more preferably between 30 to 40 MPa.

In one aspect, the polyethylene composition of the present invention has a tan delta (at angular frequency (ω) 0.157 rad/s) between 0.8 to 2.9, preferably between 0.9 to 2.8, more preferably between 0.9 to 2.6, most preferably between 1.0 to 2.5.

In one aspect, the polyethylene composition of the present invention has a molecular weight distribution between 10 to 35, preferably between 12 to 33, more preferably between 14 to 31, most preferably between 15 to 30.

In one aspect, the polyethylene composition of the present invention has MI_{21} (melt flow index at a load 21.6 kg, and a temperature of 190 °C) of from 1.0 to 70.0 g/10 min, preferably 1.0 to 60.0 g/10 min, more preferably 2.0 to 55.0 g/10 min, most preferably 2.0 to 50.0 g/10 min, or optionally preferably 2.0 to 15.0 g/10 min, determined according to ASTM D 1238 procedure A.

This invention is also related to a container article formed from the polyethylene composition of any of the above-mentioned aspects.

Preferably, the polyethylene composition of this invention is a multimodal polyethylene, preferably a bimodal polyethylene or a trimodal polyethylene.

In another embodiment, the polyethylene composition can be the a trimodal polyethylene composition comprising:

- (A) 25 to 70 % by weight of the low molecular weight polyethylene having an individual intrinsic viscosity from 0.5 to 3.0 dL/g;
- (B) 5 to 35 % by weight of the first high molecular weight polyethylene having an individual intrinsic viscosity from 2.0 to 15.0 dL/g;
- (C) 10 to 60 % by weight of the second high molecular weight polyethylene having the individual intrinsic viscosity from 2.0 to 15.0 dL/g.

In this aspect, the first high molecular weight polyethylene and the second high molecular weight polyethylene differs from each other with respect to the viscometer molecular weight thereof.

5 The first high molecular weight polyethylene and the second high molecular weight polyethylene may form together as two different fractions the second ethylene homo- or copolymer component (B).

Preferably, the polyethylene composition according to this invention may be obtained from a three stages polymerization process, preferably a slurry-slurry-slurry-process, in a reactor system comprising

- 10 (a) a first reactor;
- (b) a hydrogen removal unit arranged between the first reactor and a second reactor comprising at least one vessel connected with a depressurization equipment, preferably selected from vacuum pump, compressor, blower, ejector or a combination thereof, the depressurization equipment allowing to adjust an
- 15 operating pressure to a pressure in a range of 100 – 200 kPa (abs);
- (c) the second reactor; and
- (d) a third reactor;

the process comprising (in this sequence);

- 20 (a) polymerizing ethylene in an inert hydrocarbon medium, and optionally C₄ to C₁₂ α-olefin comonomer in the first reactor in the presence of a catalyst system, selected from Ziegler-Natta catalyst or metallocene, and hydrogen in an amount of 0.1 – 95 % by mol with respect to the total gas present in the vapor phase in the first reactor to obtain a low molecular weight polyethylene or a medium molecular weight polyethylene;
- 25 (b) removing in the hydrogen removal unit 98.0 to 99.8 % by weight, preferably from 98.0 to 99.1 % by weight of the hydrogen comprised in a slurry mixture obtained from the first reactor at a pressure in the range of 103-145 kPa (abs) and transferring the obtained residual mixture to the second reactor;
- 30 (c) polymerizing ethylene and optionally C₄ to C₁₂ α-olefin comonomer in the second reactor in the presence of a catalyst system, selected from Ziegler-Natta catalyst or metallocene, and in the presence of hydrogen in an amount obtained in step (b) to obtain a first high molecular weight polyethylene in the form of a homopolymer or a copolymer and transferring a resultant mixture to the third reactor; and
- 35 (d) polymerizing ethylene and optionally α-olefin comonomer in the third reactor in the presence of a catalyst system, selected from Ziegler-Natta catalyst or metallocene, and hydrogen, wherein the amount of hydrogen in the third reactor is in a range of 0.1 - 70% by mol, preferably 1 - 60% by mol, with respect to the total gas present in the vapor phase in the third reactor or optionally substantial absence of hydrogen to obtain a second high molecular weight polyethylene homopolymer or copolymer.
- 40 Preferably in said three stage polymerization process, the Ziegler-Natta catalyst used in this process is prepared in accordance with the method described in Hungarian patent

application number 0800771, as demonstrated in the examples thereof, such as example 1, and using triethylaluminum used as the co-catalyst.

Preferably in said three stage polymerization process, the depressurization equipment allows to adjust the operating pressure in the hydrogen removal unit to a pressure in the range of 103 – 145 kPa (abs), preferably 104 - 130 kPa (abs), most preferably 105 to 115 kPa (abs)

Preferably in said three stage polymerization process, the hydrogen removal unit further contains a stripping column for the separation of hydrogen and a liquid diluent.

Preferably in said three stage polymerization process, the removing is removing of 98.0 to 99.8 % by weight of the hydrogen, and more preferable 98.0 to 99.5 % by weight, most preferred 98.0 to 99.1 % by weight.

In said three stage polymerization process, “Substantially absence” means that hydrogen is only comprised in the third reactor in an amount which cannot be avoided by technical means.

In said three stage polymerization process, the slurry mixture obtained from the first reactor and subjected to the step of removing hydrogen in the hydrogen removal unit contains all of the solid and liquid constituents obtained in the first reactor, in particular the low molecular weight polyethylene or the medium molecular weight polyethylene. Furthermore, the slurry mixture obtained from the first reactor is saturated with hydrogen regardless of the amount of hydrogen used in the first reactor.

In said three stage polymerization process, preferably, step (a) results in the low molecular weight polyethylene or medium molecular weight polyethylene, step (c) results in the first high molecular weight polyethylene, and step (d) results in the second high molecular weight polyethylene.

In said three stage polymerization process, in case that the low molecular weight polyethylene or the medium molecular weight polyethylene, fraction (A), is a copolymer, the comonomer copolymerized together with the polyethylene may be a C₄ monomer (butene) and/or C₆ monomer (hexene). The amount of comonomer in the copolymer may be from 0.01 to 1.2 % by mol, with respect to the total amount of monomer in the polyethylene composition.

In said three stage polymerization process, in case that the first high molecular weight polyethylene, fraction (B), is a copolymer, the comonomer copolymerized together with the polyethylene may be a C₄ monomer (butene) and/or C₆ monomer (hexene). The amount of comonomer in the copolymer may be from 0.01 to 1.2 % by mol, with respect to the total amount of monomer in the polyethylene composition.

In said three stage polymerization process, in case that the second high molecular weight polyethylene, fraction (C), is a copolymer, the comonomer copolymerized together with the polyethylene may be a C₄ monomer (butene) and/or C₆ monomer (hexene). The amount of comonomer in the copolymer may be from 0.01 to 1.2 % by mol, with respect to the total amount of monomer in the polyethylene composition.

The polyethylene composition of the invention may be produced in a multistage process wherein fractions (A), (B) and (C), that is, the low molecular weight polyethylene, the first

high molecular weight polyethylene homopolymer or copolymer, and the second high molecular weight polyethylene homopolymer or copolymer, are produced in subsequent stages. In such a case, the properties of the fractions produced in the second step or the third step (or further steps) of the multistage process can either be inferred from polymers which are separately produced in a single stage by applying identical polymerisation conditions (e.g. identical temperature, partial pressures of the reactants/diluents, suspension medium, reaction time) with regard to the stage of the multistage process in which the fraction is produced, and by using a catalyst on which no previously produced polymer is present. Alternatively, the properties of the fractions produced in a higher stage of the multistage process may also be calculated, e.g. in accordance with B. Hagstrom, Conference on Polymer Processing (The Polymer Processing Society), Extended Abstracts and Final Programme, Gothenburg, August 19 to 21, 1997, 4:13.

Thus, although not directly measurable on the multistage process products, the properties of the fractions produced in higher stages of such a multistage process can be determined by applying either or both of the above methods. The skilled person will be able to select the appropriate method. One particular way of calculating the properties, such as the molecular weight (such as Mw) is applying a deconvolution process using Excel or other calculation programs. In the deconvolution process subtraction of the respective signals is carried out.

Polyethylenes, such as HDPEs, produced in a multistage process are also designated as "in- situ" blends. The resulting end product consists of an intimate mixture of the polymers from the two or three or more reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or two or three or more maxima.

The polyethylene composition may further comprise additives in amount of 0.01 to 5.0 % by weight, preferably from 0.01 to 3.0 % by weight, and more preferably 0.01 to 2.5 % by weight based on the total polyethylene composition.

The polyethylene composition further comprises at least one of a polymer processing aid, a thermal stabilizer, a slip agent, a nucleator, a flame retardant, an antioxidant, a filler, a colorant, or mixtures thereof.

In preferred embodiments "parts by weight" is "percent by weight" especially with respect to the total weight of respective mixture.

The terms and words used in the present specification and claims should not be construed as limited to ordinary or dictionary terms and should be construed in a sense and concept consistent with the technical idea of the present disclosure, based on the principle that the inventor can properly define the concept of a term to describe this invention in the best way possible.

Unless otherwise restricted, a detailed description defining or specifying the elements may be applied to all inventions and is not limited to descriptions of particular inventions. That is, the present disclosure also refers to combinations of the embodiments even if they are disclosed separately.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. The singular forms “a,” “an,” and “the” comprise plural referents unless the context clearly dictates otherwise.

5 It is to be understood that the terms such as “comprise” or “have” as used in the present specification, are intended to designate the presence of stated features, numbers, steps, operations, components, parts or combinations thereof, but not to preclude the possibility of the presence or addition of one or more other features, numbers, steps, operations, components, parts, or combinations thereof. The term “comprises” explicitly, even if not necessarily limited accordingly, includes the meaning “essentially comprising” and “consists of”.
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The term “essentially comprises” as used herein has the meaning of “comprising at least 70 %”, preferably of “comprising at least 80 %”, most preferred of “comprising at least 90 %”. If reference is made to the amount of a constituent in a mixture of material, % is wt %, relative to the total weight of the respective mixture.

15 Additionally, the terms “about” and “substantially” as used herein are used in the sense of at, or nearly at, when given the manufacturing and material tolerances inherent in the stated circumstances and are used to prevent the unscrupulous infringer from unfairly taking advantage of the present disclosure where exact or absolute figures are stated as an aid to understanding the present disclosure.

20 As used herein, “A and/or B” means “A and B, or A or B”.

The above embodiments mentioned to be preferred resulted in even more improved mechanical properties of the obtained multimodal polyethylene composition. Best results were achieved by combining two or more of the above preferred embodiments. Likewise, the embodiments mentioned above to be more or most preferred resulted in the best improvement of mechanical properties.
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DEFINITIONS AND METHODS

DEFINITIONS

As used herein, the following terms shall have the following meanings:

30 “High-density polyethylene” or “HDPE” refers to a polyethylene having a density of at least 0.940 g/cm³, preferably from 0.945 to 0.970 g/cm³.

“Intrinsic viscosity” or “IV” refers to a measure of the polymer’s molecular weight and its contribution to flow properties, determined in accordance with ISO 1628-3. Polymer samples are dissolved in decahydronaphthalene (Decalin) containing 0.2% w/v butylated hydroxytoluene (BHT) antioxidant at 150°C for 2 hours to ensure complete dissolution. The viscosity of the resulting solution is measured at 135°C, and the intrinsic viscosity is calculated using the Schultz-Blaschke equation, which correlates polymer concentration and flow behavior under dilute solution conditions. IV is expressed in deciliters per gram (dL/g).
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“Individual IV” refers to the intrinsic viscosity of the polymer fraction produced in a specific reactor within a multi-reactor polymerization process. Each reactor is configured to produce
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a distinct molecular weight fraction contributing uniquely to the overall performance of the final polyethylene composition.

“Melt Index” or “MI” refers to the rate of extrusion of a thermoplastic material through an orifice of specific length and diameter under prescribed conditions of temperature and pressure. Unless otherwise specified, MI values reported herein are measured according to ISO 1133 at 190°C, expressed in g/10 min.

“High Load Melt Index” or “MI₂₁” or “HLMI” refers to the melt index measured according to ISO 1133 at 190°C under a load of 21.6 kg, expressed in g/10 min.

“MI₁₀” refers to the melt index measured according to ISO 1133 at 190°C under a load of 10.00 kg, expressed in g/10 min.

“MI₅” refers to the melt index measured according to ISO 1133 at 190°C under a load of 5.00 kg, expressed in g/10 min.

“MI₂” refers to the melt index measured according to ISO 1133 at 190°C under a load of 2.16 kg, expressed in g/10 min.

“Density” refers to the mass per unit volume of a polymer material measured according to ASTM D1505 and is expressed in grams per cubic centimeter (g/cm³).

“Comonomer content by NMR” refers to the molar percentage of comonomer units incorporated into the polyethylene backbone determined by ¹³C-NMR.

“Parts by weight” or “percent by weight” can be used interchangeably.

“Number Average Molecular Weight” or “Mn” refers to the average molecular weight of a polymer calculated by dividing the total weight of all polymer molecules by the total number of polymer molecules. Mn is determined by gel permeation chromatography (GPC) expressed in grams per mole (g/mol).

“Weight Average Molecular Weight” or “Mw” average refers to the molecular weight that accounts for the weight contribution of each polymer molecule, giving greater emphasis to higher molecular weight species. Mw is also determined by GPC and is expressed in grams per mole (g/mol).

“Molecular weight distribution” or “MWD” is defined as the ratio of weight average molecular weight to number average molecular weight (Mw/Mn). It provides a measure of the breadth of the molecular weight distribution. A higher MWD indicates a broader distribution, which can influence processability, melt strength, and mechanical behavior.

“Z-Average Molecular Weight” or “Mz” refers to the molecular weight that gives even greater emphasis to the highest molecular weight species in the distribution. Mz is calculated from GPC data and is particularly relevant for assessing the contribution of high molecular weight tails to melt elasticity and strain hardening.

“Mz/Mn” is defined as the ratio between z-averaged molecular weight (Mz) to number-averaged molecular weight (Mn) as determined by GPC demonstrating shear thinning for controlled parison shaping and stronger wall thickness uniformity

“The first ethylene homo- or co- polymer component (A)” refers to the portion of the polyethylene composition having a molecular weight between 15,000 to 90,000 g/mol.

"The second ethylene homo- or co- polymer component (B)" refers to the portion of the polyethylene composition having a molecular weight between 300,000 to 1,100,000 g/mol.

" $\eta(0.1)$ " refers to a complex shear viscosity measured at 190°C and $\omega = 0.1$ rad/s representing low-shear melt strength and elastic recovery

5 " $\eta(100)$ " refers to a complex shear viscosity measured at 190°C and $\omega = 100$ rad/s representing high-shear flowability and extrusion efficiency

"G'" refers to a storage modulus measured at 190°C representing the elastic (energy-storing) part.

10 "G''" refers to a loss modulus measured at 190°C representing the viscous (energy-dissipating) part.

"Tan delta" refers to a ratio between loss and storage modulus at corresponding angular frequency.

"SHT" refers to strain hardening modulus determined according to ISO-18488:2015(E)

15 "Environmental Stress Crack Resistance" or "ESCR" refers to the ability of a plastic to resist cracking when subjected to chemical agents and mechanical stress simultaneously, measured according to ASTM D1693.

20 "Relaxation time" refers to the characteristic time required for a polymer melt to dissipate stress following deformation under oscillatory shear. It is a measure of melt elasticity and viscoelastic response, and is particularly relevant for evaluating parison stability and sag resistance in container articles.

METHODS

Intrinsic Viscosity (IV):

25 Intrinsic Viscosity is performed in accordance with ISO 1628-3. The polymer samples are dissolved in Decahydronaphthalene (Decalin) containing 0.2% w/v antioxidant (BHT) at a temperature of 150°C for 2 hours to ensure complete dissolution. Subsequently, the viscosity of the solution is measured at 135°C and the resulting intrinsic viscosity (IV) is calculated using the Schultz-Blaschke equation for polymer's molecular weight and flow properties under the specified conditions.

Individual molecular weight calculation and individual intrinsic viscosity:

30 The multimodal polyethylene composition of the invention is produced in a multistage process wherein fractions (A), (B) and (C) are produced in subsequent stages. In such a case, the properties of the fractions produced in the second step or the third step (or further steps) (also referred to as "individual properties") of the multistage process can either be inferred from polymers which are separately produced in a single stage by applying identical polymerization conditions (e.g. identical temperature, partial pressures of the reactants/diluents, suspension medium, reaction time) with regard to the stage of the multistage process in which the fraction is produced, and by using a catalyst on which no previously produced polymer is present. Alternatively, the properties of the fractions produced in a higher stage of the multistage process may also be calculated, e.g. in accordance with B. Hagstrom, Conference on Polymer Processing (The Polymer

40

Processing Society), Extended Abstracts and Final Programme, Gothenburg, August 19 to 21, 1997, 4: 13.

Thus, although not directly measurable on the multistage process products, the properties of the fractions produced in higher stages of such a multistage process can be determined by applying either or both of the above methods. The skilled person will be able to select the appropriate method.

Polymer HDPEs produced in a multistage process are also designated as "in- situ" blends. The resulting end product consists of an intimate mixture of the polymers from the three or more reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or two or three or more maxima.

The individual IV of each example in reactors 1, 2, and 3 is shown in Table 1.

Melt Index (MI₂ / MI₅ / MI₁₀ / MI₂₁)

The Melt Flow Index (MI) of the polymer is determined using Procedure A as specified in ISO 1133-1:2022. Polymer samples are tested under controlled conditions, precisely maintained at a temperature of 190°C, with applied loads of 2.16 kg, 5 kg, 10 kg, and 21.6 kg, commonly designated as MI₂, MI₅, MI₁₀, and MI₂₁, respectively. The MI values obtained from these procedures quantitatively represent the polymer's flowability characteristics under the defined testing parameters. The results are recorded and expressed in units of grams per 10 minutes (g/10 min). Calibration and validation of the equipment and method are performed prior to testing to ensure accurate and reliable measurement outcomes.

Density

The density of polyethylene (PE) is measured according to ASTM D1505 using a liquid column gradient tube method. The test specimens are prepared exclusively from the extrudate obtained during the Melt Index (MI) test, conducted at 190°C under a 2.16 kg load in accordance with ASTM D1238. The extrudate is cut into segments with a length of 3 mm for testing. Prior to measurement, the specimens are annealed at 100°C to ensure consistency. Density determination is performed by observing the sinking level of the 2.5 mm extrudate segments within the gradient tube, in comparison with standards of known density. Calibration using certified density standards is conducted to maintain measurement accuracy, and results are reported in units of g/cm³.

Comonomer content by ¹³C-NMR

Comonomer content was determined using carbon-13 nuclear magnetic resonance (¹³C NMR) spectroscopy. A polymer sample (180 mg) was dissolved in a solvent mixture of 2 mL trichlorobenzene and 1 mL 1,1,2,2-tetrachloroethane-d₂ at 130 °C for 2 hours to obtain a clear solution, using a 10 mm NMR tube from the (Wilmad-LabGlass, USA). The polymer solution was analyzed using a 500 MHz NMR spectrometer (Bruker ASCEND™, Bruker BioSpin AG, Switzerland), operating at 125.7 MHz for ¹³C, equipped with a cryogenic 10 mm probe. The ¹³C NMR spectrum was acquired at 120 °C using an inverse-gated decoupling

pulse sequence (zgig) with a 90° pulse angle and a delay time (D1) of 10 seconds. A minimum of 60 scans was used to achieve a signal-to-noise ratio of at least 6,000, calculated from the signal range of 28.8–31.2 ppm and the noise range of 50.0 – 70.0 ppm. The spectrum, processed using Bruker TopSpin 3.7.0, was subjected to baseline correction, phase correction, and chemical shift calibration using the C δ + peak set at 30.0 ppm as reference.

The comonomer content (%mol of comonomer) was calculated based on the following equation, using the integrated areas of assigned peaks:

$$\% \text{ mol of comonomer} = \frac{100 \times [(I_{\alpha\delta+} + I_{\beta\delta+})/2 + I_{CH}]/3}{[(I_{\alpha\delta+} + I_{\beta\delta+})/2 + I_{CH}]/3 + [(I_{\alpha\delta+}/2) + I_{\beta\delta+} + I_{\gamma\delta+} + I_{\delta\delta+}]/2}$$

- Wherein *I* represent the integral area of the corresponding carbon peaks. The peak assignments were made according to literature-reported values (for example, see, Sahoo, S. K.; Zhang, T.; Reddy, D. V.; Rinaldi, P. L. "Multidimensional NMR Studies of Poly(ethylene-co-1-butene) Microstructures" *Macromolecules* **2003**, 36, 4017.; Randall, J. C.; Hsieh, E. T. "Monomer Sequence Distribution in Ethylene-1-Hexene Copolymers" *Macromolecules* **1982**, 15, 5, 1402.), with chemical shifts (in ppm) for each assigned carbon types C $\alpha\delta$ +, C $\beta\delta$ +, C $\gamma\delta$ +, and C_{CH} located at approximately 34.1, 27.4, 30.5, and 39.7 ppm, respectively.

Molecular Weight and Molecular Weight Distribution

- Molecular weight and molecular weight distribution can be determined according to well-known literature (see, for example, Andre' M. Striegel, et. al., Modern Size-Exclusion Liquid Chromatography (Practice of Gel Permeation and Gel Filtration Chromatography), A John Wiley & Sons, INC., publication, 2009 [Chapter 8 Page 202]). For clarity, in this invention, molecular weights, including number average molecular weight (M_n), weight average molecular weight (M_w), and z-average molecular weight (M_z), are measured by the high temperature gel permeation chromatography (HT-GPC or herein called GPC) with online IR5 detector, from Polymer Char, Valencia, Spain. Freshly distilled 1,2,4-trichlorobenzene (TCB) containing 300 ppm butylated hydroxytoluene (BHT) is used as the mobile phase. The sample is taken from 3-4 random positions in a sample container (for powder form), for pellets, the sample is taken from at least 10 pellets. The sample is then cut into small pieces and randomly mixed. The sample weight of 8 mg is added into a 10-mL vial, then placed in the autosampler of GPC. Subsequently, 8 mL of TCB are added to the sample vial. The GPC autosampler is set at 160 °C and dissolving polymer with gentle shaking for 90 min. To prevent degradation during sample dissolution, approximately 8 mg BHT is added to the sample vial, and the vial headspace is filled with dry Nitrogen (N₂) after solvent addition. The BHT peak is used as a flow marker in data processing for molecular weight calculation; for long-term consistency, the flow marker is used to correct the pump flow rate. The flow marker (FM) is controlled to be within 0.5% of the nominal FM determined during column calibration. Then, 200 µL polymer solution is filtrated through an online filter (built-in) and a

guard column (PLgel 10 μ m Guard 50 x 7.5 mm; Agilent Technologies, USA). Separation is performed using three PLgel-Olexis columns in series (300 mm x 7.5 mm, 13 μ m particle size; Agilent Technologies, USA) at a flow rate of 0.5 mL/min. The column and detector compartment temperatures are maintained at 145 °C and 160 °C, respectively. Column calibration is performed using fourteen narrow molecular weight distribution Polystyrene (PS) standards (Polymer Standards Service GmbH, PSS, Mainz, Germany) having peak molecular weights (Mp) ranging from 682 g/mol to 12,000,000 g/mol. These standards are grouped into four separate mixtures for calibration. Each mixture contains standards with peak molecular weights separated by at least one decade. The total mass of each mixture is approximately 16 mg for mixtures containing 3 PS standards, and not exceeding 24 mg for mixtures containing 4 PS standards. Individual PS standards are included in each mixture at approximately 3 mg to 6 mg, with lower masses used for standards having higher Mp. Each PS mixture is dissolved in 8 mL of TCB at 160 °C for 30 minutes with gentle shaking. To prevent degradation during the dissolution of the PS standards, a procedure consistent with that of the sample preparation is followed. Approximately 8 mg of BHT is added to serve as both an antioxidant and a flow marker. Additionally, the vial headspace is filled with dry nitrogen (N₂) after solvent addition. To calculate molecular weight of polyethylene (PE), the Mark-Houwink calibration method is implemented. [1] The calibration curve is generated by fitting the elution volume versus the peak molecular weights (Mp) of the Polystyrene (PS) standard mixtures using a third-order polynomial equation. The MW calculation utilizes the generated PS calibration curve and the following Mark-Houwink (MH) parameters for TCB at 145 °C: exponent Alpha (α) = 0.722 for PS and 0.725 for PE; MH constant for PS (K_{PS}) = 0.0001016 dL/g; and MH constant for PE (K_{PE}) = 0.0004416 dL/g. The molecular weight for polyethylene (M_{PE}) corresponding to an elution volume slice with a polystyrene molecular weight (M_{PS}) on the calibration curve is calculated according to the following equation:

$$M_{PE} = \left[\frac{K_{PS}}{K_{PE}} (M_{PS})^{(\alpha_{PS}+1)} \right]^{1/(\alpha_{PE}+1)}$$

Data processing for calibration curve generation and molecular weight plot, including average molecular weight (Mn, Mw, and Mz) calculation is performed using GPC One™ software (Polymer Char). The mass constant for IR6 detector is determined by using PE52K of 2 mg/mL (Nominal Mw = 52000 g/mol) obtained from American Polymer Standards (USA). The standard PE52K is prepared and measured with similar conditions earlier described for polymer samples. Molecular weight data is considered to be applicable when the GPC measurement exhibited a calculated mass recovery greater than 95%.

35 Molecular weight deconvolution (Flory method)

The first ethylene homo- or co- polymer component (A) and the second ethylene homo- or co- polymer component (B) of inventive polymers are determined by mathematically deconvoluting the overall molecular weight distribution obtained from GPC, plotted as $dw/d\log M$ versus $\log M$. According to the presence of multiple components in the molecular weight distributions of inventive and comparative polymers, the data is deconvoluted using a model comprising the sum of nine Flory's most probably distributions (see, for example, Soares, J. B. P. An Overview of Important Microstructural Distributions for Polyolefin Analysis. *Macromolecular Symposia* **2007**, 257 (1), 1–12.) where the specific functional form used for a single component in this deconvolution, expressed as $w(\log M)_i$, is given by Equations below for $w(\log M)_i$ and $W(\log M)$:

$$w(\log M)_i = 2.30259 \times \left(\frac{M}{M_{n,i}} \right)^2 \exp\left(-\frac{M}{M_{n,i}}\right)$$

$$W(\log M) = \sum_{i=1}^9 a_i \times w(\log M)_i$$

where i is the number of distributions, ranging from 1 to 9, $M = 10^{\log M}$ is the molecular weight corresponding to $\log M$. In the equation (1), $M_{n,i}$ is the number average molecular weight of distribution i , where $M_{w,i}/M_{n,i} = 2$. The equation $W(\log M)$ represents the overall distribution by the sum of 9 distributions, and a_i represents the weight fraction (area) of distribution i .

For this fitting process, the $\log M$ axis is defined with 601 equally spaced points, spaced by 0.01, extending between 2 and 8. This range of $\log M$ values represents a molecular weight range from 10^2 to 10^8 (where log denotes the base 10 logarithm). The deconvolution is performed using a non-linear regression fitting the sum of nine such functions (each following the form of Equation 1) to the experimental data points. This fitting is done via Microsoft Excel™ 2019 Solver, employing a GRG nonlinear method with a convergence criterion of 0.001. A constraint is imposed such that the fitted weight fraction (area) of each individual distribution must be greater than 0.02. Herein, all deconvolution fits consistently yielded R -squared values greater than 0.995 when compared to the experimental data.

The nine fitted individual distributions are grouped to determine the first ethylene homo- or co- polymer component (A) and the second ethylene homo- or co- polymer component (B) fractions. The first ethylene homo- or co- polymer component (A) is defined as the sum of the five lowest molecular weight distributions among the nine fitted peaks (ordered by their molecular weight peak position). The second ethylene homo- or co- polymer component (B) is defined as the sum of the four highest molecular weight distributions among the nine fitted peaks.

The total weight fraction for the first ethylene homo- or co- polymer component (A) is the sum of the fitted weight fractions (areas) of its five corresponding distributions. Similarly, the total weight fraction for the second ethylene homo- or co- polymer component (B) is the sum of the fitted weight fractions of its four corresponding distributions.

The number average (M_n) and weight average (M_w) molecular weights for the first ethylene homo- or co- polymer component (A) and the second ethylene homo- or co- polymer component (B) groups are calculated using standard numerical summation formulas, presented as Equations (3) and (4). For each group, the calculated $dw/d\log M$ value at each discrete $\log M$ point j across the defined range (2 to 8), denoted as w_j , and the corresponding molecular weight $M_j = 10^{\log M_j}$ are used in following formulas:

$$M_n = \frac{\sum w_j}{\sum w_j / M_j}$$

$$M_w = \frac{\sum w_j M_j}{\sum w_j}$$

The summation is performed over all j points within the defined $\log M$ range.

10 Rheological Properties

Rheological properties of inventive and comparative polymers, including, Storage Modulus (G'), Loss Modulus (G''), Viscoelastic Relaxation Time (τ), Tan Delta (δ), and Viscosity Ratio ($\eta(0.1)/\eta(100)$) are conducted using a rotational rheometer, the MCR302 (Anton Paar, Graz, Austria), equipped with a 25 mm parallel plate geometry. A polymer sample is prepared by compression molding at a temperature of 190 °C for a duration of 9 minutes (4 min pre-heated and 5 minutes compressed) to form a uniform disc-shaped specimen. The sample is molded under moderate pressure and cooled under load (50 bar) to minimize internal stresses and morphological inconsistencies. The final specimen has a diameter of 25 mm and a thickness of 1.2 - 1.5 mm.

All tests are performed under a nitrogen atmosphere to prevent oxidative degradation of the polymer during thermal exposure. Prior to testing, a zero-gap procedure is performed at the measurement temperature of 190 °C to calibrate the measurement distance. The measurement gap between parallel plates is set to 1 mm. For the test procedure, after setting the temperature to 190 °C, the sample is placed on the plate and the gap is set to 1.025 mm. Excess sample material is trimmed, and temperature is allowed to reach the equilibrium around 5 min. Then the gap is carefully adjusted to the final measurement distance of 1.0 mm before the measurement is initiated.

The viscoelastic properties of the sample are evaluated using small-amplitude oscillatory shear (SAOS) testing. The sample is subjected to a frequency sweep ranging from 0.01 to 600 rad/s at a constant temperature of 190 °C and a constant strain of 5%. This strain value was confirmed to be within the linear viscoelastic (LVE) region of the material. The storage modulus (G') and loss modulus (G'') are recorded as functions of angular frequency (ω).

These moduli represent the elastic and viscous components of the polymer melt, respectively.

Relaxation time at $\omega = 0.01$ rad/s ($\tau_{0.01}$)

- 5 The relaxation time at an angular frequency $\omega = 0.01$ rad/s (radians per second), denoted as $\tau_{0.01}$, is derived from the general expressions for G' and G'' described by a single Maxwell model Macosko CW (Rheology: Principles, Measurements, and Applications, 1994, Chapter 3). The calculation uses the experimental G' and G'' values measured at $\omega = 0.01$ rad/s according to the following equation:

$$\tau = \frac{G'}{\omega \times G''} \text{ at } \omega = 0.01 \text{ rad/s}$$

- 10 Where G' and G'' is the storage and loss moduli in pascals (Pa), respectively. The measurement is performed within the linear viscoelastic regime (LVE). This calculation quantifies the material's longest relaxation processes, particularly when the response at this low frequency is dominated by a single relaxation mode, which is characteristic of the terminal zone.

- 15 Tan delta ($\tan \delta$) at $\omega = 0.157$ rad/s

Tan delta ($\tan \delta$), defined as the ratio of the loss modulus to the storage modulus shown in equation below, is a dimensionless parameter that quantifies the relative dominance of viscous versus elastic behavior in the polymer melt.

$$\tan \delta = \frac{G''}{G'}$$

- 20 The value at a specific angular frequency (ω) of 0.157 rad/s, is calculated by interpolating the direct tan delta data using Rheoplus software (Anton Paar).

Shear Viscosity

- 25 To evaluate steady shear viscosity from oscillatory data, the Cox–Merz rule is applied. The complex viscosity $\eta^*(\omega)$ obtained from the frequency sweep is interpreted as equivalent to the steady shear viscosity $\eta(\dot{\gamma})$ at a shear rate $\dot{\gamma} = \omega$. Viscosities at shear rates of 0.1 s^{-1} and 100 s^{-1} are calculated by interpolation using Rheoplus software (Anton Paar) to yield $\eta(0.1)$ and $\eta(100)$. The individual viscosity values are reported in Pascal-seconds (Pa·s). The ratio $\eta(0.1)/\eta(100)$ serves as a measurement of shear thinning behavior.

Strain hardening test (SHT)

This tensile testing method provides accurate determination of the mechanical properties of polymeric materials, specifically focusing on strain hardening modulus ($\langle G_p \rangle$) used ISO 18488:2015 specifies a standardized test method for the determination of the strain hardening modulus ($\langle G_p \rangle$) of polyethylene (PE) materials.

- 5 The methodology involves subjecting precisely prepared compression-molded test specimens to a uniaxial tensile test under controlled conditions. Key aspects of the test include:

Polyethylene sample is compression-molded into sheets of 0.30 mm thickness at a molding temperature of 180 °C, followed by annealing at 120 °C for one hour, then cool down with
10 cooling rate 1.5 °C/min to room temperature (in this case 30°C). A test specimen of defined geometry in ISO18488:2015 is punched from the compressed sheet, and its initial width and thickness are measured with a micrometer (control ± 0.03 mm).

The tensile test is conducted at an elevated temperature of 80 °C (± 1 °C). A pre-stress of 0.4 MPa is applied, and the specimen is then extended at a constant traverse speed of 20
15 mm/min.

Load and elongation are continuously measured by a Class 1 load cell and a Class 1 extensometer (with non-contact preferred for thinner specimens). The draw ratio (λ) is calculated as the ratio of current length to initial gauge length, and true stress (σ_{true}) is derived from the measured force and initial cross-sectional area, assuming volume
20 conservation.

The strain hardening modulus ($\langle G_p \rangle$) is determined from the true stress-draw ratio curve. Specifically, $\langle G_p \rangle$ is calculated as the slope of the linear regression fit of the Neo-Hookean constitutive model ($\sigma_{\text{true}} = \langle G_p \rangle * (\lambda^2 - 1/\lambda) + C$) within the critical draw ratio range of 8 to 12. A fit accuracy (R^2) greater than 0.9 is required.

- 25 The Universal Testing Machine employed was regularly calibrated using certified standards, ensuring high accuracy, repeatability, and validity of measurement results. Data from these tests provides essential insights into the polymeric materials' mechanical behavior, enabling informed decisions regarding material selection and application suitability in industrial settings.

30 Environmental Stress Crack Resistance (ESCR)

The environmental stress-cracking resistance (ESCR) of polyethylene (PE) is evaluated in accordance with ASTM D1693-21, Condition B, using a 10% (v/v) aqueous solution of Igepal CO-630 as the surface-active agent. Test specimens are prepared by compression

molding the polyethylene material into flat sheets in accordance with ASTM D4703-16, utilizing a molding temperature of 177°C to ensure uniformity and reproducibility of the specimen properties. After molding, the sheets are cut into specimens with dimensions of 38 mm × 13 mm × (1.84–1.97) mm using a blanking die with sharp, square edges. Each specimen is then notched on one surface to a depth of 0.30–0.40 mm using a calibrated notching jig, following the requirements specified in ASTM D1693-21.

Prior to testing, the specimens are conditioned for 48 hours. The notched specimens are bent and mounted in stainless steel specimen holders, and subsequently immersed in test tubes filled with the 10% Igepal CO-630 solution, ensuring complete submersion. The sealed tubes are transferred to a constant temperature bath maintained at 50 ± 0.5°C.

The specimens are periodically examined for the presence of cracks originating from the notched area. The time to failure is defined as the period elapsed until a crack visible to the naked eye appears. The result is reported as the time at which 50% of the tested specimens (F_{50}) exhibit failure, as determined by direct observation, in accordance with ASTM D1693-21.

This procedure provides a quantitative measure of the polymer's resistance to environmental stress cracking under the specified conditions of specimen preparation and test environment.

Catalyst preparation

Preparation of a solid catalyst composition

To a 1-liter flask equipped with magnetic stirrer, 10 g (0.105 mol) of magnesium chloride, 100 ml of hexane, and 51 ml (0.325 mol) of 2-ethylhexyl alcohol were introduced. The reaction mixture was then blanketed with nitrogen atmosphere. The reaction was performed by heating to 100°C, and stirred for 3 hours to produce a homogeneous solution. The solution was then cooled to a temperature of 50°C. After the homogeneous solution was cooled to 50°C, 12.5 ml (0.037 mol) of titanium butoxide was added into the homogeneous solution. The resulting mixture was then stirred at 50°C for another 2 hours to produce or obtain a slurry product. Then, 51 ml (0.47 mol) of titanium tetrachloride was dripped into the slurry product at 0°C over 1 hour period with stirring. After the addition of titanium tetrachloride was completed, the temperature was maintained at 0°C for a further 1 hour to form a solid reaction product. The temperature of the solid reaction product was then elevated from 0°C to 50°C over a period of 1 hour. 3 ml (0.027 mol) of tetraethylorthosilicate was then added to the above reactants to form a mixture. The temperature of the mixture was then raised to 80°C over a period of 1 hour. The temperature of the mixture was then maintained at 80°C for 2 hours with stirring. The resulting solid product was then separated by hot decanter, treated with 200 ml of hexane, and sufficiently washed with hexane at

ambient temperature until no trace of titanium component in the supernatant was found. The resulting catalyst composition is then used without further purification. The atomic molar-ratio of titanium to magnesium in the obtained catalyst component was 0.21.

Polymerization conditions (in large-scale reactors)

- 5 Polymerization was carried out in a continuous process using one, two, or three reactors having the reactor sizes from 200 L to 400 m³, connected in series, depending on the polymer design and its intended application. The catalyst was prepared as described above. The amounts of ethylene and hydrogen were adjusted to achieve the desired polymer composition and intrinsic viscosity in the first reactor.
- 10 The polymer slurry from the first reactor was depressurized before being transferred to the second reactor in which the unreacted gas has been removed. The polymerization in the second reactor is continued by feeding the ethylene that was set so that the polymer composition achieved the desired value. Optionally, C₄ to C₁₂ α -olefin comonomer was also fed in the second reactor for producing copolymer.
- 15 The polymer slurry from the second reactor was then transferred to the third reactor. The polymerization in the third reactor is continued by feeding the ethylene that was set so that the polymer composition achieved the desired value. Optionally, C₄ to C₁₂ α -olefin comonomer was also fed in the third reactor for producing copolymer. Optionally, hydrogen was fed to control intrinsic viscosity of the third reactor to the desired value.
- 20 The inventive and comparative examples were prepared following to the process conditions explained in Table 1.

Inventive Examples

Inventive Example 1 (IE1)

- 25 Inventive example 1 (IE1) is the multimodal polyethylene composition with blending ratio (44/24/32) in the large-scale reactor using the protocol disclosed above and the amounts of reactants as shown in Table 1. A polyethylene homopolymer was produced in the first reactor to obtain a low molecular weight portion. The low molecular weight polymer was then transferred to the second reactor to produce the first high molecular weight polyethylene. Finally, the polyethylene mixture obtained this way was transferred from the
- 30 second reactor to the third reactor to create a second high molecular weight polymer. The second and third reactors were operated under hydrogen depleted polyethylene polymerization and 1-butene comonomer was fed into the reactors to improve strain hardening property. The multimodal polyethylene composition according to IE1 has an IV of 3.0 dl/g with 1-butene comonomer content, 0.71 mol%.

Inventive Example 2 (IE2)

Inventive example 2 (IE2) was carried out in the same manner as IE1 with different blending composition (44/28/28). The inventive example 2 (IE2) with IV of 3.0 dl/g with the highest butene-1 comonomer content, 0.71 mol% was obtained.

Inventive Example 3 (IE3)

Inventive example 3 (IE3) was carried out in the same manner as IE1 with different blending composition (55/27/18). Inventive example 3 (IE3) with IV of 4.0 dl/g with the highest 1-butene comonomer content, 0.37 mol% was obtained.

Comparative Example

- 5 Comparative Example 1 (CE1) was carried out in the same manner as IE1 with different blending composition (48/10/42). The comparative example 1 (CE1) with IV of 2.07 dl/g with the highest 1-butene comonomer content, 0.42 mol% was obtained.

- 10 Comparative Example 2 (CE2) was carried out in the same manner as IE1 with different blending composition (49/25/26). The comparative example 2 (CE2) with IV of 4.36 dl/g with the highest 1-butene comonomer content, 0.10 mol% was obtained.

15 Comparative Example 3 (CE3) was carried out in the same manner as IE1 with different blending composition (44/28/28). The comparative example 3 (CE3) with IV of 3.30 dl/g with the highest 1-butene comonomer content, 0.41 mol% was obtained.

Results and Discussions

- 15 Inventive Examples IE1 to IE3 and Comparative Examples CE1 to CE3 were polymerized using a multi-reactors polymerization process, as detailed in Table 1. The process involved a 3-reactors process, designed to produce a bimodal molecular weight distribution. The final polymer was characterized and deconvoluted using gel permeation chromatography (GPC) with the physical properties, density, and comonomer content as shown in table 2.
- 20 The molecular weight distribution (Mw/Mn), and Mz/Mn ratio was obtained from the gel permeation chromatography (GPC) measurement of the final product (Table 2). Also, the first ethylene homo- or co- polymer component (A) and the second ethylene homo- or co-polymer component (B) were determined by deconvolution of the GPC curve using Flory distribution functions (Table 2), allowing precise quantification of the molecular segments responsible for melt strength and flowability.
- 25 From Table 3, it can be seen that all Inventive Examples IE1 to IE3 shows a tan delta (at $\omega = 0.157$) of around 1.3 to 1.7, which shows that the inventive compositions have viscous-liquid behavior, the $\eta(0.1)/\eta(100)$ of around 30 to 40 also confirmed that the inventive polymer compositions show viscous-liquid behavior under shear stress. From Table 4, all
- 30 inventive examples exhibit excellent performance on ESCR test results with apparently well controlled relaxation time ($\tau_{0.01}$) when compared to the Comparative Examples. From the test properties in Table 3 and Table 4, the inventors found the surprising effect which allows the polymer to maintain high ESCR while achieving ideal relaxation times for blow molding. The result is a material that can be easily extruded into complex shapes without
- 35 compromising long-term durability—a dual performance that is difficult to achieve in conventional HDPE grades.

Table 1. Polymerization condition

		Unit	CE1	CE2	CE3	IE1	IE2	IE3
Polymer composition	W _A (%)	%	48	49	44	44	44	55
	W _B (%)	%	10	25	28	24	28	27
	W _C (%)	%	42	26	28	32	28	18
Catalyst	Catalyst Feed	kg Cat / tonC2 total	0.0116	0.02320	0.0873	0.0821	0.0718	0.0624
First Reactor	P total	bar	7.65	3.8	5.27	4.87	4.69	3.75
	C2 feed	kg C2 / tonC2 total	480.16	490.17	440.00	439.85	439.85	549.90
	H2 feed	kgH2 / tonC2 Rx1	2.2080	0.4245	1.9392	1.5305	1.5218	0.7556
	Temp	°C	80	85	85	85	85	84
	Individual IV	dL/g	0.51	1.37	0.68	0.70	0.70	1.30
Second Reactor	P total	bar	3.62	3.04	3.23	3.14	3.09	2.57
	C2 feed	kgC2 / tonC2 total	99.81	249.72	280.01	240.05	280.05	270.04
	Temp	°C	73	80	66	75	75	75
	Comonomer type		1-butene	1-butene	1-butene	1-butene	1-butene	1-butene
	Comonomer feed	kgC4 / tonC2 Rx2	63.70	0	2.96	48.45	42.01	21.03
	Individual IV	dl/g	5.96	11.49	8.19	4.67	6.11	8.90
	IV	dl/g	1.45	4.79	3.6	2.10	2.80	3.80
Third Reactor	P total	bar	2.77	3.94	2.50	2.06	2.43	2.14
	C2 feed	kgC2 / tonC2 total	420.03	260.11	279.98	320.10	280.10	180.06
	Temp	°C	75	80	68	77	77	77
	Comonomer type		1-butene	1-butene	1-butene	1-butene	1-butene	1-butene
	Comonomer feed	kgC4 / tonC2 Rx3	21.18	1.03	3.27	11.06	9.64	31.99
	H2 feed	kgH2 / tonC2 Rx3	0.0243	0.0768	0.0870	0.0166	0.0280	0.0254
	Individual IV	dl/g	2.93	3.14	2.53	4.60	3.51	4.91
	IV	dl/g	2.07	4.36	3.3	2.90	3.00	4.00

Table 2. Physical properties and deconvolution calculation

Properties		Unit	CE1	CE2	CE3	IE1	IE2	IE3
Physical Properties	MI ₂₁	g/ 10 min		2.41	6.53	8.21	9.00	3.5
	MI ₁₀	g/ 10 min		0.37		1.47	1.57	0.53
	MI ₅	g/ 10 min		0.08		0.37	0.39	0.13
	MI _{2.1}	g/ 10 min	1.08			0.09	0.09	0.03
	Density (anneal 100 °C)	g/cm ³	0.957	0.955	0.953	0.948	0.948	0.948
	Comonomer		1-butene	1-butene	1-butene	1-butene	1-butene	1-butene
	Comonomer content (NMR)	% mol	0.42	0.10	0.41	0.71	0.71	0.37
GPC	Mw of component (A)	g/mol	19,200	68,000	35,400	41,400	39,900	54,800
	Mw of component (B)	g/mol	283,700	1,186,800	817,200	591,800	617,200	785,100
	Mw	g/mol	135,100	455,200	361,500	242,400	258,500	307,700
	Mn	g/mol	9,500	18,500	11,800	11,800	12,000	19,800
	Mw/Mn		14	25	30	20	22	15
	Mz	g/mol	834,100	3,076,500	2,757,900	1,400,000	1,621,300	1,775,000
	Mz/Mn		88	166	234	119	135	90

*Mw of component (A) : Mw of the first ethylene homo- or co- polymer component (A); Mw of component (B) : Mw of the second ethylene homo- or co- polymer component (B)

Table 3. Mechanical properties

Properties	Unit	CE1	CE2	CE3	IE1	IE2	IE3
Tan delta (at $\omega = 0.157$ rad/s)	Pa	3.01	0.759	1.206	1.711	1.535	1.32
η (0.1) / η (100)		8.1	43	32	18	22	29
SHT	MPa	15.0	22.9		34.0	31.0	39.0
η (0.01)	Pa·s	17,796	697,014	323,350	138,511	201,108	352,840
G' (0.01)		95	3,850	1,728	570	722	1,665
G'' (0.01)		429	5,814	2,733	1,287	1,492	3,163

Table 4. Final properties

Properties	Unit	CE1	CE2	CE3	IE1	IE2	IE3
ESCR (10% Igepal, F50 condition B)	hr.	96	240		> 4,000	> 4,000	> 4,000
Relaxation time ($t_{0.01}$)	sec	19	66	63	44	48	53

Claims

1. A polyethylene composition comprising:
 - a first ethylene homo- or co- polymer component (A) having a weight average molecular weight (Mw) of from 15,000 to 90,000 g/mol determined as set forth in the description; and
 - a second ethylene homo- or co- polymer component (B) having a weight average molecular weight (Mw) of 300,000 to 1,100,000 g/mol determined as set forth in the description;wherein the polyethylene composition has
 - a density from 0.940 to 0.975 g/cm³ measured by ASTM D 1505;
 - a MI₂₁ (melt flow index at load 21.6 kg and temperature of 190°C) from 1.0 to 70 g/10 min measured by ASTM D 1238;
 - a ratio Mz/Mn is from 80 to 200, determined as set forth in the description; and
 - a tan delta (at angular frequency (ω) of 0.157 rad/s) from 0.8 to 2.9, determined as set forth in the description.
2. The polyethylene composition according to claim 1, wherein polyethylene composition has a comonomer content of 0.01 to 1.20 mol%, determined as set forth in the description, with respect to the total amount of the polyethylene composition.
3. The polyethylene composition according to any one of claims 1 to 2, wherein the comonomer is selected from the group consisting of C₃ to C₁₂ α -olefin comonomer selected from the group consisting of 1-butene or 1-hexene, or mixture thereof.
4. The polyethylene composition according to any one of the preceding claims, wherein the first ethylene homo- or co- polymer component (A) has a weight average molecular weight (Mw) of from 15,000 to 80,000 g/mol, determined as set forth in the description.
5. The polyethylene composition according to any one of the preceding claims, wherein the second ethylene homo- or co- polymer component (B) has a weight average molecular weight (Mw) of from 350,000 to 1,100,000 g/mol, determined as set forth in the description.
6. The polyethylene composition according to any one of the preceding claims, wherein the polyethylene composition has an Environmental Stress Crack Resistance (ESCR) of at least 4,000 hours, determined as set forth in the description.
7. The polyethylene composition according to any one of the preceding claims, wherein the polyethylene composition has a SHT from 25 to 50 MPa, determined as set forth in the description, determined as set forth in the description.
8. The polyethylene composition according to any one of the preceding claims, wherein the polyethylene composition a molecular weight distribution from 10 to 35, determined as set forth in the description.

9. The polyethylene composition according to any one of the preceding claims, wherein the polyethylene composition has MI_{21} (melt flow index at a load 21.6 kg, and a temperature of 190 °C) of from 1.0 to 60.0 g/10 min, determined as set forth in the description.
10. A container article formed from the polyethylene composition of any one of the preceding claims.