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(71) Applicant: **Borealis Technology Oy**
06101 Porvoo (FI)

(72) Inventors:
- **Bergstra, Michiel Friso**
  00810 Helsinki (FI)
- **Eriksson, Erik Johan Gunnar**
  00810 Helsinki (FI)
- **Pakkanen, Britt Anneli**
  01120 Västerskog (FI)
- **Gustafsson, Bill Benjamin Rudolf**
  44441 Stenungsund (SE)
- **Weickert, Günter**
  48683 Ahaus (DE)

(74) Representative: **Korsten, Marius et al**
Arnold & Siedsma
Sweelinckplein 1
NL-2517 GK Den Haag (NL)

(54) Multimodal polyethylene co-polymer resin composition, a preparation process therefore and a polymeric product comprising the same

(57) The present invention relates to a multimodal polyethylene co-polymer resin composition comprising (a) a lower molecular weight (LMW) ethylene polymer fraction and (b) a higher molecular weight (HMW) ethylene copolymer fraction, wherein the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b1) a higher molecular weight (HMW) ethylene co-polymer subfraction having a weight average molecular weight at least 2 times the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, which (b1) higher molecular weight (HMW) ethylene co-polymer subfraction amounts from about 1-30 wt% of the total amount of the multimodal polyethylene co-polymer resin composition and comprises comonomers in amount of at least about 1 wt% of the total amount of comonomer present in said multimodal polyethylene copolymer resin composition, a process for its preparation and its use.

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Description

[0001] The present invention relates to a multimodal polyethylene co-polymer resin composition comprising a lower molecular weight ethylene polymer (LMW) fraction and a higher molecular weight ethylene polymer (HMW) fraction, and to a process for preparing the above mentioned multimodal polyethylene co-polymer resin composition, and to a polymeric product comprising and/or made from the above mentioned multimodal polyethylene co-polymer resin composition.

[0002] The term "multimodal" means herein, unless otherwise stated, multimodality with respect to molecular weight distribution and includes also bimodal polymer.

[0003] Usually, a polyethylene comprising at least two polyethylene fractions, which have been produced under different polymerization conditions resulting in different (weight average) molecular weights and molecular weight distributions for the fractions, is referred to as "multimodal". The prefix "multi" relates to the number of different polymer fractions present in the polymer. Thus, for example, multimodal polymer includes so called "bimodal" polymer consisting of two fractions. The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as a function of its molecular weight, of a multimodal polymer will show two or more maxima or is typically distinctly broadened in comparison with the curves for the individual fractions. 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 form typically together a broadened molecular weight distribution curve for the total resulting polymer product.

[0004] Traditionally, a cascade of reactors is used wherein different reaction conditions are applied during the catalytic polymerization in order to obtain a broad multimodal molecular weight distribution. By using a cascade of reactors it is possible to produce an ethylene polymer resin composition comprising a lower molecular weight (LMW) fraction and a higher molecular weight (HMW) fraction. However, when the higher molecular weight fraction is produced, the co-monomer concentration in the higher molecular weight part decreases with increasing molecular weight. Furthermore, the higher molecular weight (HMW) fraction typically has also an influence on the mechanical properties of a final polymer so that e.g. with said high molecular weight (HMW) fraction i.e. environmental stress crack resistance (ESCR) can be controlled.

[0005] Multimodal polyethylene compositions produced in a multistage process and comprising at least a low molecular weight (LMW) fraction and a high molecular weight (HMW) fraction may sometimes comprise polymer particles of "very high molecular weight",i.e. gels, defined e.g. as the "white spots" in the prior art literature, which particles can cause inhomogeneities in the composition and the end-products produced thereof.

[0006] A first object of the present invention is to provide a multimodal polyethylene co-polymer resin composition for use in various product applications, with improved mechanical properties, such as improved environmental stress cracking properties.

[0007] A second object of the present invention is to provide a multimodal polyethylene co-polymer resin composition which, depending on the properties that are variable within the product window of the invention, enables further, desirable alternatives for different end applications of the multimodal polyethylene resin composition, with desirable, even improved, polymer properties over the prior art products.

[0008] Another object is to provide a process for producing a multimodal polyethylene co-polymer resin composition, which process enables to obtain the multimodal product with advantageous properties, such as advantageous mechanical properties and/or good homogeneity between the particles with respect to molecular weight distribution in industrially feasible production rates.

[0009] A first aspect of the present invention relates to multimodal polyethylene co-polymer resin composition comprising (a) a lower molecular weight (LMW) ethylene polymer fraction and (b) a higher molecular weight (HMW) ethylene co-polymer fraction, wherein (b) the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b1) a higher molecular weight (HMW) ethylene co-polymer subfraction having a weight average molecular weight at least 2 times the weight average molecular weight (Mw) of said multimodal polyethylene co-polymers resin composition, which (b1) higher molecular weight (HMW) ethylene co-polymer subfraction amounts from about 1-30 wt% of the total amount of the multimodal polyethylene co-polymer resin composition and comprises comonomers in amount of at least about 1 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

[0010] Due to the fact that the higher molecular weight ethylene co-polymer fraction of the resin composition comprises the subfraction (b1), which subfraction (b1) has a relatively high molecular weight and a relatively high amount of comonomers the mechanical properties of the resin composition are improved. This is particularly noticeable in end products prepared from this resin composition e.g. in terms of an increased resistance to environmental stress cracking (ESCR). The higher molecular weight (HMW) fraction typically comprises ethylene co-polymers having an average molecular weight greater than 500.000.

[0011] The higher molecular weight (HMW) ethylene co-polymer subfraction (b1) comprises preferably about 1-20

wt%, more preferably up to 15 wt% of the total amount of the (co-)polymer resin.

[0012] Preferably, the higher molecular weight (HMW) ethylene co-polymer subfraction (b1) comprises up to 30 wt%, more preferably between 3-25 wt%, even more preferably between 5 and 20 wt% of the total amount of co-monomer. Higher molecular weight ethylene co-polymers comprising an amount co-monomer within the claimed ranges provide highly feasible properties to the end products.

[0013] In a preferred embodiment (b) the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b2) a very high molecular weight (VHMW) ethylene co-polymer subfraction, which very high molecular weight (VHMW) subfraction comprises ethylene co-polymers having a weight average molecular weight at least 3 times of the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, and which very high molecular weight (VHMW) ethylene co-polymer subfraction amounts of from about 0.5-15 wt% of said multimodal polyethylene co-polymer resin composition.

[0014] The (b2) very high molecular weight (VHMW) subfraction typically comprises ethylene co-polymers having an average molecular weight greater than 1.000.000.

[0015] The (b2) very high molecular weight (VHMW) subfraction has a co-monomer content of about 3-20 wt%, preferably about 5-20 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

[0016] The total amount of co-monomer present in the multimodal polyethylene co-polymer resin composition is 20 wt% or less, preferably between about 0.1 and 15 wt%, more preferably between about 0.1 and 10 wt%.

[0017] As co-monomer, olefins with 3-20 carbon atoms including (C3-C20) alpha-olefins and preferably (C3-C12) alpha-olefins are used. Particular preferred co-monomers are propene, 1-butene, 1-hexene, 1-octene, and mixtures thereof.

[0018] Preferably, (a) the lower molecular weight (LMW) ethylene polymer fraction comprises ethylene homo- and/or co-polymers.

[0019] The comonomer distribution as defined in claim 1 provides the inventive effect of the multimodal polyethylene co-polymer resin of the invention, i.e. good mechanical properties and/or homogeneity as mentioned above. The other properties of the multimodal polyethylene of the invention are not critical and can vary considerably within the scope of the claim 1. Thus said other properties, such as density, melt flow rate, molecular weight distribution etc. can be chosen and adapted depending on the desired end application of the multimodal polyethylene co-polymer resin of the invention. E.g. the following preferable subgroups of multimodal polyethylene co-polymer resin composition are given. The density of the multimodal polyethylene co-polymer resin is preferably more than 900 kg/m^3, more preferably more than 915 kg/m^3. The upper limit of said density is not limited and can be e.g. up to 960 kg/m^3 depending on the end application of the multimodal polyethylene co-polymer resin composition.

[0020] Preferably, the MFR_2 of the multimodal polyethylene co-polymer resin composition may be less than or equal to 100 g/10 min, preferably less than equal to 50 g/10 min. The lower limit of said MFR_2 is not limited and may be e.g. at least 0.001 g/10 min or more, again depending on the end application of the multimodal polyethylene co-polymer resin composition.

[0021] The multimodal polyethylene co-polymer resin composition may comprise further polyethylene homo- or co-polymer fractions. In one preferable embodiment the multimodal polyethylene co-polymer resin composition consists of (a) a low molecular weight (LMW) ethylene homo- or co-polymer fraction and (b) a high molecular weight (HMW) ethylene co-polymer fraction, whereby said (b) high molecular weight (HMW) ethylene co-polymer fraction comprises (b1) a high molecular weight (HMW) ethylene co-polymer subfraction, and/or preferably (b2) a very high molecular weight (VHMW) ethylene co-polymer subfraction as defined above or below, or in the claims, and optionally a subfraction b3, which is formed by the part of the (b) high molecular weight fraction that does not belong to the high molecular weight subfraction (b1) and very high molecular weight subfraction (b2).

[0022] Further preferably, the polydispersity index (Mw/Mn; referred herein as PDI) of the multimodal polyethylene co-polymer resin composition is more than 3, more preferably more than 5. The upper limit of said PDI is not limited and may be e.g. up to 50 depending on the end application of the multimodal polyethylene co-polymer resin composition.

[0023] A second aspect of the present invention relates to a process for the preparation of a multimodal polyethylene co-polymer resin composition comprising the steps of:

i) polymerizing ethylene monomers, and optionally one or more co-monomers, in the presence of a catalyst to obtain (a) a lower molecular weight (LMW) ethylene polymer fraction; and

ii) polymerizing ethylene monomers and one or more comonomers, in the presence of the polymerization product of the first polymerization step and of a catalyst to obtain (b) a higher molecular weight (HMW) ethylene co-polymer fraction, wherein the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b1)a higher molecular weight (HMW) ethylene co-polymer subfraction having a weight average molecular weight at least 2 times the weight average molecular weight (Mw) of said multimodal polyethylene co-polymers resin composition, which (b1) higher molecular weight (HMW) ethylene co-polymer subfraction amounts from about 1-30 wt% of the total amount of the

multimodal polyethylene co-polymer resin composition and comprises comonomers in amount of at least about 1 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

[0024] By carrying out the process of the invention a multimodal polyethylene co-polymer resin composition is obtained having a higher average molecular weight fraction that comprises a relatively high amount of co-monomer. Such a relatively high amount of co-monomer in the HMW-fraction of the resin composition provides products produced thereof with improved mechanical properties.

[0025] The higher molecular weight (HMW) fraction typically comprises ethylene co-polymers having an average molecular weight greater than 500.000.

[0026] Further, the (b1) higher molecular weight (HMW) ethylene co-polymer subfraction comprises preferably about 1-20 wt% of the total amount of the co-polymer resin.

[0027] The (b1) higher molecular weight (HMW) ethylene co-polymers subfraction comprises up to 30 wt%, preferably about 3-25 wt% of the total amount of co-monomer.

[0028] In a preferred embodiment, the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b2) a very high molecular weight (VHMW) ethylene co-polymer subfraction, which very high molecular weight (VHMW) subfraction comprises ethylene co-polymers having a weight average molecular weight at least 3 times of the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, and which very high molecular weight (VHMW) ethylene co-polymers amounts from about 0.5-15 wt% of the said multimodal polyethylene co-polymer resin composition.

[0029] The higher molecular weight fraction typically comprises ethylene co-polymers having a weight average molecular weight greater than 1.000.000.

[0030] More preferably, the very high molecular weight (VHMW) ethylene co-polymers subfraction has a co-monomer content of about 3-20 wt%, preferably about 5-20 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

[0031] The total amount of co-monomer present in the multimodal polyethylene co-polymer resin composition is 20 wt% or less, preferably between about 0.1 and 15 wt%, more preferably between about 0.1 and 10 wt%.

[0032] As co-monomer preferably an alpha-olefin co-monomer is used. More preferably (C3-C20) alpha-olefins and even more preferably (C3-C12) alpha-olefins are used. Particular preferred co-monomers are 1-butene, 1-hexene, 1-octene, and mixtures thereof.

[0033] Preferably, (a) the lower molecular weight (LMW) ethylene polymer fraction comprises ethylene homo-or co-polymer.

[0034] The choice of the catalyst for producing the multimodal polyethylene co-polymer resin of the invention is not critical. As polymerization catalyst a Ziegler-Natta catalyst, single site catalyst including metallocene-based catalyst and non-metallocene, which both terms are well known in the art, or chromium based catalyst may be used. According to one embodiment a Ziegler-Natta catalyst is preferred.

[0035] The choice of the Ziegler-Natta catalyst is not critical. Typically said Ziegler-Natta catalyst may contain a magnesium compound, an aluminium compound and a titanium or zirconium compound, optionally supported on a particulate support.

[0036] Thus, the catalysts include coordination catalysts of a transition metal compound of group 4 to 10 of the Periodic Table (IUPAC) or a compound of an actinide or lanthanide, such as Ziegler-Natta (ZN), metallocenes, non-metallocenes, Cr-catalysts etc. The catalyst may be supported, e.g. with conventional supports including silica, Al-containing supports and magnesium dichloride based supports. Preferably the catalyst is a ZN catalyst, more preferably the catalyst is non-silica supported ZN catalyst), and most preferably $MgCl_2$-based ZN catalyst.

[0037] The Ziegler-Natta catalyst further preferably comprises a group 4 (group numbering according to new IUPAC system) metal compound, preferably titanium, more preferably chlorine-containing titanium compound, magnesium dichloride and aluminium.

[0038] The catalyst may be commercially available or be produced in accordance or analogously to the literature. For the preparation of the preferable catalyst usable in the invention reference is made to W02004055068 and W02004055069, WO2003106510 and EP 0 810 235. The content of these documents in its entirety is incorporated herein by reference, in particular concerning the general and all preferred embodiments of the catalysts described therein as well as the methods for the production of the catalysts. Particularly, preferred Ziegler-Natta catalysts are described in EP 0 810 235.

[0039] The multimodal polyethylene co-polymer resin composition may be produced by two or more stage polymerisation or by the use of two or more different polymerisation catalysts and/or by the use of different polymerisation conditions in a one stage polymerisation. In principle any polymerisation method including slurry and gas phase polymerisation can be used for producing polymers. The temperature in the polymerisation reactor needs to be sufficiently high to reach an acceptable activity of the catalyst. On the other hand, the temperature should not exceed the softening temperature of the polymer.

[0040] Preferably, however, the polymers are produced in a two or three stage polymerisation. Suitable polymerisation processes include liquid phase polymerisation, e.g. slurry polymerization, preferably in the presence of a diluent (or optionally carried out in bulk), or gas phase polymerisation. Preferably the polymerisation involves at least one slurry polymerisation (e.g. in a loop reactor).

[0041] The above mentioned low molecular weight (LMW) ethylene polymer fraction or high molecular weight (HMW) ethylene polymer fraction may be polymerized as a slurry polymerization (e.g. in a slurry tank or loop reactor) and the other as a gas phase polymerization (e.g. in a fluidized bed reactor), in any order.

[0042] Particularly preferably the multimodal polyethylene co-polymer resin composition is formed at least in a two stage process comprising a slurry loop polymerisation followed by a gas phase polymerization. A preferred loop reactor-gas phase reactor system usable in this invention is generally known as BORSTAR® process. The multistage polymerization is preferably carried out using the same Ziegler-Natta catalyst system in each stage. Moreover, the low molecular weight (LMW) polymer fraction is preferably polymerized in the slurry reactor, preferably in a loop reactor, and the high molecular weight (HMW) polymer fraction in the gas phase reactor in the presence of the reaction product of the slurry reactor. As such loop-gas phase reactor systems reference is made to EP 517 868, EP 797 599 and W02004/111095.

[0043] The conditions used in such processes are well known. For slurry reactors, the reaction temperature will generally be in the range 60 to 110 °C (preferably 85-110 °C), the reactor pressure will generally be in the range 5 to 80 bar, and the mean residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100 °C. Preferred diluents include hydrocarbons such as propane, isobutane or hexane. Hydrogen is also preferably fed into the reactor to function as a molecular weight regulator.

[0044] If gas phase reactions are employed then conditions are preferably as follows:

- the temperature is within the range of 50°C to 130°C, preferably between 60°C and 115 °C,
- the pressure is within the range of 10 bar to 60 bar, preferably between 10 bar to 40 bar,
- hydrogen can be added for controlling the molar mass in a manner known per se,
- the mean residence time is typically 0.5 to 8 hours.

[0045] The gas used will commonly be a non-reactive gas such as nitrogen or low boiling point hydrocarbons such as propane together with monomer (e.g. ethylene), co-monomer (e.g. propene, 1-butene, 1-hexene, etc) and a molecular weight regulator (e.g. hydrogen). If desired, the polymerisation may be carried out in a known manner under supercritical conditions in the slurry, preferably loop reactor, and/or as a condensed mode in the gas phase reactor.

[0046] The reaction mixture is preferably removed from the first reactor either continuously or intermittently. Preferably hydrogen, residual monomer and inert low boiling hydrocarbon medium are removed from the reaction mixture. The removal of hydrogen, low boiling hydrocarbon is preferably carried out by flashing means.

[0047] After the reaction mixture has been removed from the first reactor and hydrogen, residual reactants and inert low boiling hydrocarbon medium are also removed, the ethylene polymers formed are fed into the second reactor in step ii). In this second reactor the ethylene polymers formed in step i) are preferably fed into a fluidized bed and a moving bed, wherein the residence time in the fluidized bed and time of a particle for a single pass through the moving bed are independently controlled. This allows for an optimal degree of freedom for the adjustment of required properties of the polymer particles formed. A single pass time through the moving bed is about 5 - 360 s, more preferable 10 - 250 s.

[0048] The time for the particle to do a single pass through the moving bed is independently controlled, i.e. plug flow reactor (PFR), of the gas phase reactor residence time. The integrated combination of the moving bed (PFR) and the fluidized bed reactor results in a narrower split distribution between the (b2) very high molecular weight (VHMW) fraction and the (b) high molecular weight (HMW) fraction compared to two cascaded reactors. Particles which contain a very large weight fraction of very high molecular weight molecules (b2) cannot exist; particles having made a large amount of passes through the moving bed have also made the same amount of passes through the fluidized bed. The residence time distribution for particles in the fluidized bed is behaving like a Continuous Stirred Tank Reactor (CSTR).

[0049] Preferably, the fluidized bed and the moving bed are integrated into one reactor.

[0050] According to a preferred embodiment the time for a particle for a single pass through the moving bed is independently controlled, preferably by the outflow rate of polymeric materials from the moving bed.

[0051] In the moving bed the catalytic polymerization conditions are different compared to those in the fluidized bed.

[0052] First, because the bed of catalytic particles has a higher density in the moving bed section of the reactor. Furthermore, in order to apply different polymerization conditions, one preferred solution is that gas with a different composition than in the fluidized bed is fed directly into the moving bed. Another, more preferred way of controlling the catalytic polymerization conditions is the use of a separation medium in order to create different polymerization conditions.

[0053] For example, a polymerization is carried out at a lower concentration of a chain-growth terminating agent such as hydrogen. Feeding a separating medium to the moving bed results in different reaction conditions in the fluidized bed and in the moving bed.

[0054] Preferably the separation medium is added into the moving bed and forms an extraction zone for the undesired gases, the particulate polymeric material is allowed to pass through the separation medium and settles in the form of the moving bed. The separation medium may be a gas or a liquid. The separation medium may be inert to the catalytic polymerization such as nitrogen and C1 - C12 alkanes.

[0055] The separation medium may be reactive such as monomer, comonomer such as C_2-C_{12}-alkene or mixtures thereof. Mixtures of inert and catalytic polymerization reactive separation medium may be used as desired.

[0056] Preferably, use is made of a separation medium which is a liquid that evaporates under the condition during the catalytic polymerization in the moving bed. Accordingly, during evaporation a gas extraction zone of separating medium is formed.

[0057] The addition of separation medium and/or separate feed of the reactants to both the fluidized bed and the moving bed may be such that in the fluidized bed and/or in the moving bed a condensed mode polymerization occurs which is beneficial to productivity.

[0058] It is further preferred that the separation medium comprises a polymerization monomer or comonomer or mixture thereof.

[0059] Before the first polymerization in the first reactor takes place, a pre-polymerisation is preferably carried out.

[0060] A third aspect of the present invention relates to a multimodal polyethylene co-polymer resin composition obtainable by the above mentioned process. In a preferred embodiment of the invention the polymerization process is an in situ polymerization process, comprising preferably a gas phase polymerization in a fluidized bed and in a moving bed. More preferably, the combination of a gas phase polymerization in said fluidized and moving bed is effectuated in two reaction zones arranged in one reactor system. Said combination of a gas phase polymerization in a fluidized and a moving bed, results in multimodal polyethylene co-polymer resin composition wherein the particles show an improved homogeneity with respect to weight average molecular weight distribution.

[0061] A last aspect of the present invention relates to the use of a multimodal polyethylene co-polymer resin composition as described above for the production of a polymeric product.

[0062] Mentioned and other features and advantages of the process and the reactor system according to the invention are further explained by way of several examples given for illustrative purposes and without the intention to limit the invention thereto.

Examples

I. Definitions and measurement methods

[0063] MFR_2, MFR_5 and MFR_{21} measured according to ISO 1133 at 190°C at loads of 2.16, 5.0, and 21.6 kg respectively.

[0064] Molecular weights (Mn, Mw), molecular weight distribution (referred herein polydispersity index as PDI)

[0065] Mw, Mn and Mw/Mn (=PDI) are measured by SEC according to the following method:

Weight average molecular weight (Mw), number average molecular weight (Mn) and thus molecular weight distribution (PDI = Mw/Mn) was determined by size exclusion chromatography (SEC) based on standard test methods ISO 16014-2:2003 and ISO 16014-4:2003. The molecular weight averages and molecular weight distribution were measured on a Waters Alliance GPCV2000 SEC instrument with on-line viscometer at 140 degrees Celsius using 1,2,4-trichlorobenzene (TCB) stabilized with 2,6-di-tert-butyl-4-methylphenol (BHT) as an eluent. A set of two mixed beds and one 107 Å TSK-Gel columns from TosoHaas was used and the system was calibrated with NMWD polystyrene standards (from Polymer laboratories).

SEC FTIR

[0066] The comonomer concentration as function of the molecular weight is measured by SEC FTIR. The separated polymer fractions from the size exclusion chromatography (SEC) are transferred to a LC transformer. The LC transformer sprays the fractionated polymer solution on a rotating Germanium disc at a temperature of 140°C and a pressure below 10 TORR. The disc with the fractionated polymer, by molecular mass, is analyzed by FTIR. The relative amount of methyl- end groups are obtained as function of the molecular mass

SEC:	Waters 150CV plus
Detector:	Refractive index (RI)- and Visc.- detector
Calibration:	Narrow standard PS (A1114_new1114)

(continued)

Columns:	3X PL Mixed B.
LC-transform:	Series 300 from Lab Connections
FTIR:	Perkin-Elmer GX

[0067] Density of the materials is measured according to ISO 1183:1987 (E), method D, using compression moulded plaque samples with isopropanol-water as gradient liquid. The cooling rate of the plaques when crystallising the samples was 15 C/min. Conditioning time was 16 hours.

[0068] Comonomer content (mol%) was determined with Fourier transform infrared spectroscopy (FTIR) after calibration against C13-NMR results. The comonomer content was converted from mol percent (mol%) to weight percent (wt%).

Polymerization examples

[0069] The catalyst used in polymerization examples was Lynx 200 TM catalyst as manufactured and supplied by Engelhard Corporation, Pasadena, USA.

[0070] The Ziegler-Natta catalyst is weighed and activated with 1 ml of TEA / hexane solution (3 mol/L). The catalyst is mixed in bed of dried NaCl. The catalyst salt mixture is added to a 100 ml reactor. The used reactor is a tubular like gas phase reactor with a distribution plate on the bottom. Gas is passing once through the reactor, so the gas phase reactor is operated without gas circulation. The catalyst salt mixture is dried in the gas phase reactor under a nitrogen flow.

[0071] The polymerization is started by feeding a monomer mixture. 1-Hexene is fed as vapour via a saturated ethylene flow (0,8 g/g).

Comparative example

[0072] The polymerization is executed at 80°C and at atmospheric pressure.

[0073] The first polymerization step for 1200 s is a homo polymerization of ethylene with a Hydrogen / Ethylene ratio of 3 / 7 (molar ratio).

[0074] The second polymerization step for 600 s is a copolymerization of ethylene with 1-hexene. The 1-hexene / ethylene ratio is 1 / 50, and the hydrogen / ethylene ratio is 3 / 7.

Example 1

[0075] The polymerization is executed at 80°C and at atmospheric pressure. The first polymerization step for 336 s is a homo polymerization of ethylene with a Hydrogen / Ethylene ratio of 17 / 3. The second polymerization step for 24 s is a copolymerization of ethylene with 1-hexene. The 1-hexene / ethylene ratio is 1 / 5, and the hydrogen / ethylene ratio is 3 / 7. The third polymerization step is a repetition of the first polymerization step; a 336 s lasting a homo polymerization of ethylene with a Hydrogen / Ethylene ratio of 17 / 3. The fourth polymerization step is a repetition of the second polymerization step; a 24 s lasting ethylene 1-hexene copolymerization. The 1-hexene / ethylene ratio is 1 / 50, and the hydrogen / ethylene ratio is 3 / 7. The fifth polymerization step is repetition of the first polymerization step. The sixth polymerization step is a repetition of the second polymerization step. The seventh polymerization step is repetition of the first polymerization step. The eight polymerization step is a repetition of the second polymerization step. The ninth polymerization step is repetition of the first polymerization step. The tenth polymerization step is a repetition of the second polymerization step.

[0076] In this example the catalyst has 'moved' 5 times through the moving bed.

Example 2

[0077] The polymerization is executed at 80°C and at atmospheric pressure. The first polymerization step for 336 s is a homo polymerization of ethylene with a Hydrogen / Ethylene ratio of 17 / 3. The second polymerization step is repetition of the first polymerization step. The third polymerization step for 24 s is a copolymerization of ethylene with 1-hexene. The 1-hexene / ethylene ratio is 1 / 50, and the hydrogen / ethylene ratio is 3 / 7. The fourth polymerization step is a repetition of the first polymerization step. The fifth polymerization step is repetition of the third polymerization step. The sixth polymerization step is a repetition of the first polymerization step. The seventh polymerization step is

repetition of the third polymerization step. The eight polymerization step is a repetition of the first polymerization step. The ninth polymerization step is repetition of the third polymerization step. The tenth polymerization step is a repetition of the third polymerization step.

[0078] In this example the catalyst has 'moved' 4 times through the moving bed.

Table 1

MW	**Example 1**		**Example 2**		**Comparative Example**	
g/mol	**Relative amount of CH3 groups**	**Cumulative wt% polymer**	**Relative amount of CH3 groups**	**Cumulative wt% polymer**	**Relative amount of CH3 groups**	**Cumulative wt% polymer**
5000	0,028	7,0	0,022	6,9	0,058	2,3
6300	0,023	10,7	0,019	10,4	0,040	3,8
10000	0,023	17,4	0,037	17,1	0,034	7,2
15800	0,021	27,8	0,018	27,5	0,027	13,4
31600	0,020	38,9	0,019	38,8	0,022	21,6
39800	0,021	44,0	0,020	44,0	0,019	26,0
50100	0,021	49,1	0,021	49,2	0,017	30,8
63100	0,022	55,8	0,022	56,1	0,018	37,6
79400	0,025	60,6	0,024	61,1	0,018	42,9
100000	0,026	68,1	0,025	68,7	0,018	52,1
158500	0,027	74,8	0,028	75,5	0,016	61,0
199500	0,025	80,5	0,031	81,2	0,018	69,2
316200	0,031	90,9	0,029	91,5	0,022	84,8
1000000	0,046	96,8	0,033	97,2	0,024	94,0
1259000	0,052	98,1	0,035	98,3	0,026	95,9
1585000	0,062	99,1	0,049	99,0	<0,01	100,0

Table 2

	Example 1	**Example 2**	**Comparative example**
Co-monomer concentration (wt%)	6,5	6,6	0,6
Mn (g/mol)	19 400	19 900	42 700
Mw (g/mol)	241 600	242 600	376 500
PDI=Mw/Mn (-)	12,5	12,2	8,8
2xMw (g/mol)	483 200	485 200	753 000
3xMw(g/mol)	724 800	727800	1129500

[0079] From the results provided in table 1, one can draw the conclusion that the polymer resins of Example 1 & 2 contain in the fraction having an Mw below 16 kD about 40% less co-monomer compared to the comparative example. In the fraction having a Mw between 16 kD to 40 kD the resins of examples 1 and 2 comprise about the same concentration co-monomer as the comparative example. In the fraction between 50 kD and 100 kD the examples 1 and 2 comprise about 30% more co-monomer compared to the comparative example. In the fraction between 100 kD and 1000 kD the examples 1 and 2 contain respectively 50% and 60% more co-monomer compared to the comparative example. In the fraction above 1.000 kD examples 1 and 2 comprise respectively 130% and 225% more co-monomer compared to the

comparative example.

[0080] It is thus clear from the examples above that the polymer resin composition of examples 1 and 2 comprise a relatively high amount of co-monomer in the higher molecular weight fraction. This means that products thereof have increased mechanical properties, such as for example an increased environmental stress cracking of moulded pipes.

Claims

1. Multimodal polyethylene co-polymer resin composition comprising (a) a lower molecular weight (LMW) ethylene polymer fraction and (b) a higher molecular weight (HMW) ethylene co-polymer fraction, wherein the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b1) a higher molecular weight (HMW) ethylene co-polymer subfraction having a weight average molecular weight at least 2 times the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, which (b1) higher molecular weight (HMW) ethylene co-polymer subfraction amounts from about 1-30 wt% of the total amount of the multimodal polyethylene co-polymer resin composition and comprises comonomers in amount of at least about 1 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

2. Multimodal polyethylene co-polymer resin composition according to claim 1, wherein (b1) the higher molecular weight (HMW) ethylene co-polymer subfraction comprises about 1-20 wt% of the total amount of the co-polymer resin.

3. Multimodal polyethylene co-polymer resin composition according to claim 1 or 2, wherein (b1) the higher molecular weight (HMW) ethylene co-polymer subfraction comprises about up to 30 wt%, preferably about 3-25 wt% of the total amount of co-monomer.

4. Multimodal polyethylene co-polymer resin composition according to any of the claims 1-3, wherein the (b) higher molecular weight(HMW) ethylene co-polymer fraction comprises(b2) a very high molecular weight (VHMW) ethylene co-polymer subfraction, which (b2) very high molecular weight (VHMW) subfraction comprises ethylene co-polymers having a weight average molecular weight at least 3 times of the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, and which (b2) very high molecular weight (VHMW) ethylene co-polymer subfraction amounts of from about 0.5-15 wt% of said multimodal polyethylene co-polymer resin composition.

5. Multimodal polyethylene co-polymer resin composition according to claim 4, wherein (b2) the very high molecular weight (VHMW) ethylene co-polymer subfraction has a comonomer content of about 3-20 wt%, preferably about 5-20 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

6. Multimodal polyethylene co-polymer resin composition, according to any of the claims 1 -5, wherein the total amount of co-monomer present in the multimodal polyethylene co-polymer resin composition is about 20 wt% or less, preferably about 0.1-15 wt%, more preferably about 0.1-10 wt%.

7. Multimodal polyethylene co-polymer resin composition according to any of the claims 1-6, wherein the co-monomer is an (C3-C20) alpha-olefin co-monomer.

8. Multimodal polyethylene co-polymer resin composition according to claim 7, wherein the co-monomer is propene, 1-butene, 1-hexene, 1-octene or mixtures thereof.

9. Multimodal polyethylene co-polymer resin composition according to any of the claims 1-8, wherein (a) the lower molecular weight (LMW) ethylene polymer fraction comprises ethylene homo- or co-polymers.

10. Multimodal polyethylene co-polymer resin composition according to any of the claims 1-9, wherein the MFR_2 of the multimodal polyethylene co-polymer resin composition is less that 100 gram per 10 minutes, preferably less than 50 gram per 10 minutes, more preferably between 100 gram per 10 minutes and 0.001 gram per 10 minutes.

11. Multimodal polyethylene co-polymer resin composition according to any of the claims 1-10, wherein the polydispersity index (Mw/Mn) of the multimodal polyethylene co-polymer resin composition is more than 3, preferably more than 5, more preferably between 3 and 50.

12. Process for the preparation of a multimodal polyethylene co-polymer resin composition comprising the steps of:

i) polymerizing ethylene monomers, and optionally one or more co-monomers, in the presence of a catalyst to obtain (a) a lower molecular weight (LMW) ethylene polymer fraction; and
ii) polymerizing ethylene monomers and one or more co-monomers, in the presence of the polymerization product of the first polymerization step and of a catalyst to obtain (b) a higher molecular weight (HMW) ethylene co-polymer fraction, wherein the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b1) a higher molecular weight (HMW) ethylene co-polymer subfraction having a weight average molecular weight at least 2 times the weight average molecular weight (Mw) of said multimodal polyethylene co-polymers resin composition, which (b1) higher molecular weight (HMW) ethylene co-polymer subfraction amounts from about 1-30 wt% of the total amount of the multimodal polyethylene co-polymer resin composition and comprises comonomers in amount of at least about 1 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

13. Process according to claim 12, wherein (b1) the higher molecular weight (HMW) ethylene co-polymer subfraction comprises about 1-20 wt% of the total amount of the co-polymer resin.

14. Process according to claim 12 or 13, wherein (b1) the higher molecular weight (HMW) ethylene co-polymer subfraction comprises about up to 30 wt%, preferably about 3-25 wt% of the total amount of co-monomer.

15. Process according to any of the claims 12 - 14, wherein (b) the higher molecular weight (HMW) ethylene co-polymer fraction comprises (b2) a very high molecular weight (VHMW) ethylene co-polymer subfraction, which very high molecular weight (VHMW) subfraction comprises ethylene co-polymers having a weight average molecular weight at least 3 times of the weight average molecular weight (Mw) of said multimodal polyethylene co-polymer resin composition, and which very high molecular weight (VHMW) ethylene co-polymer subfraction amounts from about 0.5-15 wt%of said multimodal polyethylene co-polymer resin composition.

16. Process according to claim 15, wherein (b2) the very high molecular weight (VHMW) ethylene co-polymer subfraction has a co-monomer content of about 3-20 wt%, preferably about 5-20 wt% of the total amount of co-monomer present in said multimodal polyethylene co-polymer resin composition.

17. Process according to any of the claims 12 -16, wherein the total amount of co-monomer present in the multimodal polyethylene co-polymer resin composition is 20 wt% or less, preferably about 0.1-15 wt%, more preferably about 0.1-10 wt%.

18. Process according to any of the claims 12-17, wherein the co-monomer is an (C3-C20) alpha-olefin co-monomer.

19. Process according to claim 18, wherein the co-monomer is propene, 1-butene, 1-hexene, 1-octene or mixtures thereof.

20. Process according to any of the claims 12-19, wherein the catalyst is selected from one or more of a Ziegler-Natta catalyst and a single site catalyst.

21. Process according to any of the claims 12-20, wherein the polymerization for obtaining the first fraction is carried out in a slurry or gas phase and optionally preceded by a prepolymerisation step.

22. Process according to any of the claims 10-21, wherein the polymerization for preparing the (b) higher molecular weight (HMW) ethylene co-polymer fraction is carried out in a fluidized bed and in a moving bed, wherein the residence time in the fluidized bed and time of a particle for a single pass through the moving bed are independently controlled.

23. Process according to claim 22, wherein the fluidized bed and the moving bed are integrated in one reactor.

24. Process according to claim 22 or 23, wherein time of a particle for a single pass through the moving bed is controlled by controlling the outflow rate of particles from the moving bed.

25. Process according to any of the claims 22-24, wherein the moving bed is separated from the fluidized bed by a separation medium.

26. Process according to any of the claims 22-25, wherein the separation medium is fed inside the moving bed.

27. Multimodal polyethylene co-polymer resin composition obtainable by the process according to any of the claims 12-26.

28. Polymeric product comprising a multimodal polyethylene co-polymer resin composition according to any of the claims 1-11 or 27.

29. Use of a multimodal polyethylene co-polymer resin composition according to any of the claims 1-11 or 27 for the production of a polymeric product.

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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