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(71) Applicant: **BOREALIS AG** [AT/AT]; Wagramer Strasse 17-19, 1220 Vienna (AT).

(72) Inventors: **TRAN, Tuan Anh**; Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz (AT). **SUMERIN, Victor**; Borealis Polymers Oy, 300A, Muovintie 19, 06850 Kulloo (FI). **KELA, Jarmo**; Borealis Polymers Oy, 300A, Muovintie 19, 06850 Kulloo (FI).

(74) Agent: **CAMPBELL, Neil**; Dehns, St Bride's House, 10 Salisbury Square, London EC4Y 8JD (AT).

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(54) Title: A PROCESS FOR PRODUCING POLYOLEFIN FILM COMPOSITION AND FILMS PREPARED THEREOF

(57) **Abstract:** The present invention deals with a process for producing a multimodal ethylene polymer composition suitable for producing films by blow moulding. The process comprises: i) copolymerising ethylene and optionally an alpha-olefin comonomer in a first polymerisation step in the presence of a silica supported Ziegler-Natta polymerisation catalyst to produce a first ethylene homo-or copolymer (PE1) having a melt flow rate MFR_2 of from 10 to < 150 g/10 min; ii) copolymerising ethylene and optionally an alpha-olefin comonomer in a second polymerisation step in the presence of the first ethylene homo- or copolymer to produce a first ethylene polymer mixture (PEM1) comprising the first ethylene homo-or copolymer and a second ethylene homo- or copolymer, said first ethylene polymer mixture having a melt flow rate MFR_2 of from 80 to 180 g/10 min, and wherein the MFR_2 of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1) and the second ethylene homo- or copolymer (PE2) has a melt flow rate MFR_2 of from 150 to 800 g/10 min and iii) copolymerising ethylene and at least one alpha-olefin comonomer in a third polymerisation step in the presence of the first ethylene polymer mixture to produce a second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture and a third ethylene copolymer (PE3), said second ethylene polymer mixture having a density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min.

A process for producing polyolefin film composition and films prepared thereof

Field of the Invention

The present invention is directed to a method for producing multimodal ethylene polymer film compositions and films prepared thereof. Especially, the present invention is directed to a method for making multimodal ethylene copolymer film composition by a process comprising polymerizing ethylene in at least three polymerization stages. Further, the present invention is directed to films comprising the multimodal ethylene copolymer composition produced by the method comprising at least three polymerization stages. Further, the invention is directed to the use of such multimodal ethylene copolymer compositions for making films with improved processability and throughput.

Related Art and Problem to Be Solved

It is known to produce ethylene copolymers suitable for producing films by copolymerizing ethylene in two polymerization stages, for instance from EP-A-691367 which discloses bimodal ethylene copolymers produced in two fluidized bed reactors.

Also WO-A-2004000902 discloses bimodal low density PE resins. The document does not disclose multimodal ethylene polymer composition produced in three polymerisation stage.

EP-A-2067799 discloses multimodal LLDPE resins which have been produced in two polymerization stages in a loop and a gas phase reactor in the presence of a ligand-modified catalyst. The document does not disclose a third polymerization stage.

EP-A-2246369 discloses LLDPE produced in the presence of a Ziegler-Natta catalyst with specific halogenated aluminium alkyl compounds as a cocatalyst. While the document briefly refers to two-stage polymerization its examples are one-stage polymerization runs. The document does not disclose any three-stage polymerization.

EP-A-2246372 discloses LLDPE produced in the presence of a Ziegler-Natta catalyst with a halogenated aluminium alkyl compounds as a cocatalyst. The document discloses ethylene copolymerisation in two-stage polymerization configuration. It’s only generally mentioned that optionally additional reactors may be used. It does not, however, disclose the nature of the polymers produced in such stages and it exemplifies only two-stage polymerization.

EP-A-2228394 discloses LLDPE polymers produced in two polymerization stages using amulticomponent catalyst comprising titanium and vanadium compounds. The document discloses that it is possible to include further polymerization stages, such as a third and a fourth polymerization stage which are preferably conducted in gas phase. It does not, however, disclose the nature of the polymers produced in such stages and it exemplifies only two-stage polymerization.

EP-A-2186833 discloses a three-stage polymerization in a cascaded reactor sequence of two loop reactors followed by a gas phase reactor. In the first stage a polymer having an MFR_2 of preferably 200 to 1000 g/10 min and a density of preferably 945 to 978 kg/m^3 is produced. The polymer produced in the second stage is disclosed to have an MFR_2 of preferably 200 to 1000 g/10 min and a density of preferably 945 to 978 kg/m^3. The final polymer had an MFR_{21} of preferably 5 to 30 g/10 min and a density of preferably 940 to 970 kg/m^3. The polymers produced in the first and second stages had the same MFR_2. In the exemplified process the polymers produced in the first two stages were homopolymers and the final resins had MFR_5 of from 0.2 to 0.4 g/10 min and density of about 955 kg/m^3.

EP2415598 discloses a multilayer film comprising at least one layer of a multimodal terpolymer, e.g. a bimodal linear low density ethylene/1-butene/C_6-C_{12}-alpha-olefin terpolymer. The multimodal polymer comprises a low molecular weight component corresponding ethylene homopolymer or a low molecular weight ethylene copolymer and a high molecular weight component corresponding to ethylene terpolymer with higher alpha-olefin comonomers. Preferably the low molecular weight component is an ethylene homoplymer and the high molecular weight component is ethylene/1-butene/1-hexene terpolymer. The multimodal terpolymer is produced in a two stage polymerisation process. Final densities are disclosed to be in the range of 910 – 950 kg/m^3 or 935 – 970 kg/m^3 or 900 – 935 kg/m^3; and MFR_{21} (190 °C, 21,6 kg load, ISO1133) 7 to 60 g/10min or 2 to 35 g/10min or 15 to 80 g/10min, respectively.

WO 2015/086812 (EP2883887) describes a process for making multimodal ethylene copolymers where the method comprises polymerising ethylene and comonomers in three polymerisation stages, and further use of said copolymers for making films. The ethylene copolymer produced according to the process has the density of 906 to 925 kg/m^3 and MFR_5 (190 °C, 5,0 kg load, ISO1133) of 0,5 to 5,0 g/10 min. The copolymer produced in the first polymerisation stage and the first homo- or copolymer mixture being a mixture of the first polymer and polymer produced in the second stage have claimed densities in the range of 945 to 955 kg/m^3 and melt flow rates MFR_2 in the range of 150 to 1000 kg/m^3.

EP2883885 describes similar type of polymers as described in WO 2015/086812.

Many unimodal or bimodal ethylene polymers have desired properties for different application needs. Suitable densities and melt flow rates are normal decisive features of polyethylene film materials. Such bimodal terpolymers are known in the state of the art and are described e.g. in WO 03/066698 or WO 2008/034630 or are commercially available, such as BorShape^{TM} FX1001 and BorShape^{TM} FX1002 (both from Borealis AG, Vienna, Austria).

Even though the basic properties (density, melt flow ratio and mechanical properties) of polyethylene composition for making films might be satisfactory with known polyethylene film compositions, there still remains a need to provide a polyethylene film composition having in addition improved throughput (output) and extrudability properties in film making processes. High throughput and/or excellent extrudability properties are very much appreciated by the film makers. Combinations of desired properties of polymer film composition, such as especially high stiffness and/or DDI and/or tear, and/or good processability with high throughput in film making process is not discussed in related art publications.

The present invention therefore provides especially for example good mechanical properties, such as for example especially high stiffness and/or optionally DDI and/or optionally tear and/or good processability and/or high throughput in a film making process.

Summary of the Invention

As seen from one embodiment of the invention the present invention provides a process for producing a multimodal ethylene copolymer film composition comprising the steps of

i) copolymerising ethylene and optionally an alpha-olefin comonomer in a first polymerisation step in the presence of a silica supported Ziegler-Natta polymerisation catalyst to produce a first ethylene homo- or copolymer (PE1) having a a melt flow rate MFR_2 of from 10 to < 150 g/10 min and optionally a density of from 940 to 980 kg/m^3 and;

(ii) copolymerising ethylene and optionally an alpha-olefin comonomer in a second polymerisation step in the presence of the first ethylene homo- or copolymer to produce a first ethylene polymer mixture (PEM1) comprising the first ethylene homo- or copolymer and a second ethylene homo- or copolymer, said first ethylene polymer mixture having a melt flow rate MFR_2 of from 80 to 180 g/10 min and optionally a density of from 940 to 980 kg/m^3 and, and wherein the MFR_2 of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1) and the second ethylene homo- or copolymer (PE2) has a melt flow rate MFR_2 of from 150 to 800 g/10min and optionally a density of from 940 to 980 kg/m^3 ; and

(iii) copolymerising ethylene and at least one alpha-olefin comonomer in a third polymerisation step in the presence of the first ethylene polymer mixture to produce a second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture and a third ethylene copolymer (PE3), said second ethylene polymer mixture having a density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min.

Detailed description

Polymerisation process

The present process for producing polyethylene film composition comprises polymerisation of ethylene and at least one α-olefin in multiple polymerisation steps in the presence of a polymerisation catalyst. In the present application definition multiple polymerisation steps mean a process comprising at least three polymerisation steps.

The at least one α-olefin or one alpha-olefin comonomer may be selected from α-olefins having from 4 to 10 carbon atoms and their mixtures. Especially suitable α-olefins are those having from 4 to 8 carbon atoms, including their mixtures. In particular 1-butene, 1-hexene and 1-octene and their mixtures are the preferred α-olefins. The α-olefin used in the different polymerisation steps may be the same or different.

The polymerisation steps may be connected in any order, i.e. the first polymerisation step may precede the second polymerisation step, or the second polymerisation step may precede the first polymerisation step or, alternatively, polymerisation steps may be connected in parallel. However, it is preferred to operate the polymerisation steps in cascaded mode.

Catalyst

The polymerisation is conducted in the presence of an olefin polymerisation catalyst. The catalyst may be any catalyst which is capable of producing all components of the multimodal ethylene copolymer. Suitable catalysts are, among others, Ziegler – Natta catalysts based on a transition metal, such as titanium, zirconium and/or vanadium or metallocene catalysts or late transition metal catalysts, as well as their mixtures. Especially Ziegler – Natta catalysts are useful as they can produce polymers within a wide range of molecular weight and other desired properties with a high productivity. Ziegler – Natta catalysts used in the present invention are supported on an external support.

Suitable Ziegler – Natta catalysts preferably contain a magnesium compound, an aluminium compound and a titanium compound supported on a particulate support.

The particulate support typically used in Ziegler-Natta catalysts comprises an inorganic oxide support, such as silica, alumina, titania, silica-alumina and silica-titania or a $MgCl_2$ based support. The catalyst used in the present invention is supported on an inorganic oxide support. Most preferably the Ziegler-Natta catalyst used in the present invention is supported on silica.

The average particle size of the silica support can be typically from 10 to 100 μm. However, it has turned out that special advantages can be obtained if the support has an average particle size from 15 to 30 μm, preferably from 18 to 25 μm. Alternatively, the support may have an average particle size of from 30 a 80 μm, preferably from 30 to 50 μm. Examples of suitable support materials are, for instance, ES747JR produced and marketed by Ineos Silicas (former Crossfield), and SP9-491, produced and marketed by Grace.

The magnesium compound is a reaction product of a magnesium dialkyl and an alcohol. The alcohol is a linear or branched aliphatic monoalcohol. Preferably, the alcohol has from 6 to 16 carbon atoms. Branched alcohols are especially preferred, and 2-ethyl-1-hexanol is one example of the preferred alcohols. The magnesium dialkyl may be any compound of magnesium bonding to two alkyl groups, which may be the same or different. Butyl-octyl magnesium is one example of the preferred magnesium dialkyls.

The aluminium compound is chlorine containing aluminium alkyl. Especially preferred compounds are aluminium alkyl dichlorides, aluminium dialkyl chlorides and aluminium alkyl sesquichlorides.

The transition metal is preferably titanium. The titanium compound is a halogen containing titanium compound, preferably chlorine containing titanium compound. Especially preferred titanium compound is titanium tetrachloride.

The catalyst can be prepared by sequentially contacting the carrier with the above mentioned compounds, as described in EP-A-688794 or WO-A-99/51646. Alternatively, it can be prepared by first preparing a solution from the components and then contacting the solution with a carrier, as described in WO-A-01/55230.

The Ziegler – Natta catalyst is used together with an activator, which is also called as cocatalyst. Suitable activators are metal alkyl compounds, typically Group 13 metal alkyl compounds, and especially aluminium alkyl compounds. They include trialkylaluminium compounds, such as trimethylaluminium, triethylaluminium, tri-isobutylaluminium, trihexylaluminium and tri-n-octylaluminium. Aluminium alkyl compounds may also include alkyl aluminium halides, such as ethylaluminium dichloride, diethylaluminium chloride, ethylaluminium sesquichloride, dimethylaluminium chloride and the like and alkylaluminium oxy-compounds, such as methylaluminiumoxane, hexaisobutylaluminiumoxane and tetraisobutylaluminiumoxane and also other aluminium alkyl compounds, such as isoprenylaluminium. Especially preferred cocatalysts are trialkylaluminiums, of which triethylaluminium, trimethylaluminium and tri-isobutylaluminium are particularly preferred.

The amount in which the activator is used depends on the specific catalyst and activator. Typically triethylaluminium is used in such amount that the molar ratio of aluminium to the transition metal, like Al/Ti, is for example from 1 to 1000, preferably from 3 to 100 and in particular from about 5 to about 30 mol/mol.

Prepolymerisation

In addition to the actual polymerisation steps, i.e. in the present invention in addition to the at least three polymerisation steps, the process may comprise a prepolymerisation step preceding the actual polymerisation steps. The purpose of the prepolymerisation is to polymerise a small amount of polymer onto the catalyst at a low temperature and/or a low monomer concentration. By prepolymerisation it is possible to improve the performance of the catalyst in slurry and/or modify the properties of the final polymer. The prepolymerisation step is conducted in slurry.

Thus, the prepolymerisation step may be conducted in a loop reactor. The prepolymerisation is then preferably conducted in an inert diluent, typically a hydrocarbon diluent such as methane, ethane, propane, n-butane, isobutane, pentanes, hexanes, heptanes, octanes etc., or their mixtures. Preferably the diluent is a low-boiling hydrocarbon having from 1 to 4 carbon atoms or a mixture of such hydrocarbons.

The temperature in the prepolymerisation step is typically from 0 to 90 °C, preferably from 20 to 80 °C and more preferably from 55 to 75 °C.

The pressure is not critical and is typically from 1 to 150 bar, preferably from 40 to 80 bar.

The amount of monomer is typically such that from about 0.1 to 1000 grams of monomer per one gram of solid catalyst component is polymerised in the prepolymerisation step. As the person skilled in the art knows, the catalyst particles recovered from a continuous prepolymerisation reactor do not all contain the same amount of prepolymer. Instead, each particle has its own characteristic amount which depends on the residence time of that particle in the prepolymerisation reactor. As some particles remain in the reactor for a relatively long time and some for a relatively short time, then also the amount of prepolymer on different particles is different and some individual particles may contain an amount of prepolymer which is outside the above limits. However, the average amount of prepolymer on the catalyst typically is within the limits specified above.

The molecular weight of the prepolymer may be controlled by hydrogen as it is known in the art. Further, antistatic additive may be used to prevent the particles from adhering to each other or the walls of the reactor, as disclosed in WO-A-96/19503 and WO-A-96/32420.

The catalyst components are preferably all (separately or together) introduced to the prepolymerisation step when a prepolymerisation step is present. However, where the solid catalyst component and the cocatalyst can be fed separately it is possible that only a part of the cocatalyst is introduced into the prepolymerisation stage and the remaining part into subsequent polymerisation stages. Also in such cases it is necessary to introduce so much cocatalyst into the prepolymerisation stage that a sufficient polymerisation reaction is obtained therein.

Typically, the amounts of hydrogen and comonomer are adjusted so that the presence of the prepolymer has no effect on the properties of the final multimodal polymer. Especially, it is preferred that melt flow rate of the prepolymer is greater than the melt flow rate of the final polymer but smaller than the melt flow rate of the polymer produced in the first polymerisation stage. It is further preferred that the density of the prepolymer is greater than the density of the final polymer. Suitably the density is approximately the same as or greater than the density of the polymer produced in the first polymerisation stage. Further, typically the amount of the prepolymer is not more than about 5 % by weight of the multimodal polymer comprising the prepolymer.

First Polymerisation Step

The first polymerisation step typically operates at a temperature of from 20 to 150 °C, preferably from 50 to 110 °C and more preferably from 60 to 100 °C. The polymerisation may be conducted in slurry, gas phase or solution. In the first polymerisation step the first homo- or copolymer of ethylene is produced. The first ethylene homo- or copolymer has a melt flow rate MFR_2 of from 10 to < 150 g/10 min and optionally a density of from 940 to 980 kg/m^3.

The catalyst may be transferred into the first polymerisation step by any means known in the art. It is thus possible to suspend the catalyst in a diluent and maintain it as homogeneous slurry. Especially preferred it is to use oil having a viscosity form 20 to 1500 mPa·s as diluent, as disclosed in WO-A-2006/063771. It is also possible to mix the catalyst with a viscous mixture of grease and oil and feed the resultant paste into the first polymerisation step. Further still, it is possible to let the catalyst settle and introduce portions of thus obtained catalyst mud into the first polymerisation step in a manner disclosed, for instance, in EP-A-428054. The first polymerisation step may also be preceded by a prepolymerisation step, in which case the mixture withdrawn from the prepolymerisation step is directed into the first polymerisation step.

Into the first polymerisation step ethylene, the α-olefin, optionally an inert diluent, and optionally hydrogen are introduced as well as optionally an alpha-olefin comonomer. Hydrogen, alpha-olefin comonomer and the α-olefin are introduced in such amounts that the melt flow rate MFR_2 and the density of the first ethylene homo- or copolymer are in the desired values.

The α-olefin or the alpha-olefin comonomer (these terms may be used interchangeably herein) is as defined above having from 4 to 10 carbon atoms and their mixtures, and especially suitable α-olefins are those having from 4 to 8 carbon atoms, including their mixtures. In particular 1-butene, 1-hexene and 1-octene and their mixtures are the preferred α-olefins.

The polymerisation of the first polymerisation step may be conducted in slurry. Then the polymer particles formed in the polymerisation, together with the catalyst fragmented and dispersed within the particles, are suspended in the fluid hydrocarbon. The slurry is agitated to enable the transfer of reactants from the fluid into the particles.

The polymerisation usually takes place in an inert diluent, typically a hydrocarbon diluent such as methane, ethane, propane, n-butane, isobutane, pentanes, hexanes, heptanes, octanes etc., or their mixtures. Preferably the diluent is a low-boiling hydrocarbon having from 1 to 4 carbon atoms or a mixture of such hydrocarbons. An especially preferred diluent is propane, possibly containing minor amount of methane, ethane and/or butane.

The ethylene content in the fluid phase of the slurry may be from 1 to about 50 % by mole, preferably from about 1.5 to about 20 % by mole and in particular from about 2 to about 15 % by mole. The benefit of having a high ethylene concentration is that the productivity of the catalyst is increased but the drawback is that more ethylene then needs to be recycled than if the concentration was lower.

The slurry polymerisation may be conducted in any known reactor used for slurry polymerisation. Such reactors include a continuous stirred tank reactor and a loop reactor. It is especially preferred to conduct the polymerisation in loop reactor. In such reactors the slurry is circulated with a high velocity along a closed pipe by using a circulation pump. Loop reactors are generally known in the art and examples are given, for instance, in US-A-4582816, US-A-3405109, US-A-3324093, EP-A-479186 and US-A-5391654.

If the first ethylene homo- or copolymer is produced in conditions where the ratio of the α-olefin to ethylene is not more than about 400 mol/kmol, such as not more than 300 mol/kmol, then it is usually advantageous to conduct the slurry polymerisation above the critical temperature and pressure of the fluid mixture. Such operation is described in US-A-5391654.

When the first polymerisation step is conducted as slurry polymerisation the polymerisation in the first polymerisation step is conducted at a temperature within the range of from 50 to 115 °C, preferably from 70 to 110 °C and in particular from 80 to 105 °C. The pressure in the first polymerisation step is then from 1 to 300 bar, preferably from 40 to 100 bar.

The amount of hydrogen is adjusted based on the desired melt flow rate of the first ethylene homo- or copolymer and it depends on the specific catalyst used. For many generally used Ziegler – Natta catalysts the molar ratio of hydrogen to ethylene is for example from 10 to 2000 mol/kmol, preferably from 20 to 1000 mol/kmol and in particular from 40 to 800 mol/kmol.

The amount of the α-olefin or alpha-olefin comonomer is adjusted based on the desired density of the first ethylene homo- or copolymer and it, too, depends on the specific catalyst used. For many generally used Ziegler – Natta catalysts the molar ratio of the α-olefin to ethylene is for example from 100 to 1000 mol/kmol, preferably from 150 to 600 mol/kmol.

The polymerisation of the first polymerisation step may also be conducted in gas phase. A preferable embodiment of gas phase polymerisation reactor is a fluidised bed reactor. There the polymer particles formed in the polymerisation are suspended in upwards moving gas. The gas is introduced into the bottom part of the reactor. The upwards moving gas passes the fluidised bed wherein a part of the gas reacts in the presence of the catalyst and the unreacted gas is withdrawn from the top of the reactor. The gas is then compressed and cooled to remove the heat of polymerisation. To increase the cooling capacity it is sometimes desired to cool the recycle gas to a temperature where a part of the gas condenses. After cooling the recycle gas is reintroduced into the bottom of the reactor. Fluidised bed polymerisation reactors are disclosed, among others, in US-A-4994534, US-A-4588790, EP-A-699213, EP-A-628343, FI-A-921632, FI-A-935856, US-A-4877587, FI-A-933073 and EP-A-75049.

According to the preferred embodiment of present invention, the polymerisation of the first polymerisation step is conducted in slurry.

Further, suitably the polymerisation is conducted at a temperature exceeding the critical temperature of the fluid mixture and pressure exceeding the critical pressure of the fluid mixture.

According to the invention at least one α-olefin or alpha-olefin comonomer may be present in the first polymerisation step, where the polymer produced in the first step is the first ethylene homo- or copolymer. Typically the density of the first ethylene homo- or copolymer may be from 940 to 980 kg/m^3. The polymerisation is preferably conducted as a slurry polymerisation in liquid diluent at a temperature of from 75 °C to 100 °C, such as from 80 to 95 °C and a pressure of from 30 bar to 100 bar, such as from 40 to 80 bar, like from 50 to 80 bar. The molar ratio of the optional α-olefin to ethylene may be for example preferably from 100 to 1000 mol/kmol, and preferably from 150 to 600 mol/kmol. This ratio may also be lower, especially when no or little α-olefin is used/added in the polymerisation step. The molar ratio of hydrogen to ethylene may be suitably from 100 to 1000 mol/kmol, preferably from 150 to 700 mol/kmol. MFR$_2$ of the first ethylene homo- or copolymer produced in the first polymerisation step is within the range 10 to < 150 g/10 min.

The polymerisation rate in the first polymerisation step is suitably controlled to achieve the desired amount of the first ethylene homo- or copolymer in the second ethylene polymer mixture. Preferably the second ethylene polymer mixture contains from 10 to 35 % by weight, preferably 13 to 26 % by weight, further preferred > 15 to < 25 % by weight of the first ethylene homo- or copolymer. The polymerisation rate is suitably controlled by adjusting the ethylene concentration in the first polymerisation step. When the first polymerisation step is conducted as slurry polymerisation in the loop reactor the mole fraction of ethylene in the reaction mixture is suitably from 2 to 10 % by mole and preferably from 3 to 8 % by mole.

According to a preferred embodiment the ratio of MFR_2(PEM1) / MFR_2(PE1) may be for example between 1 and 8, preferably between 2 and 7.5.

Second Polymerisation Step

The second homo- or copolymer of ethylene is produced in the second polymerisation step in the presence of the first homo- or copolymer of ethylene.

The second polymerisation step typically operates at a temperature of from 20 to 150 °C, preferably from 50 to 110 °C and more preferably from 60 to 100 °C. The polymerisation may be conducted in slurry, gas phase or solution. In the second polymerisation step the second homo- or copolymer of ethylene is produced in the presence of the first homo- or copolymer of ethylene. The first homo- or copolymer of ethylene (PE1) and the second homo- or copolymer of ethylene (PE2) together form the first ethylene polymer mixture (PEM1). The first ethylene homo- or polymer mixture may have for example a density of from 940 to 980 kg/m^3 and a melt flow rate MFR_2 of from 10 to < 150 g/10 min.

The first hom- or copolymer of ethylene (PE1) is transferred from the first polymerisation step to the second polymerisation step by using any method known to the person skilled in the art. If the first polymerisation step is conducted as slurry polymerisation in a loop reactor, it is advantageous to transfer the slurry from the first polymerisation step to the second polymerisation step by means of the pressure difference between the first polymerisation step and the second polymerisation step.

Into the second polymerisation step ethylene, optionally an inert diluent, and optionally hydrogen and/or the α-olefin are introduced. Hydrogen and the α-olefin, are introduced in such amounts that the melt flow rate MFR_2 and the density of the first ethylene polymer mixture are within the desired values.

The polymerisation of the second polymerisation step may be conducted in slurry in the same way as it was discussed above for the first polymerisation step.

The amount of hydrogen in the second polymerisation step is adjusted based on the desired melt flow rate of the first ethylene polymer mixture and it depends on the specific catalyst used. For many generally used Ziegler – Natta catalysts the molar ratio of hydrogen to ethylene is for example from 100 to 2000 mol/kmol, preferably from 200 to 1000 mol/kmol and in particular from 250 to 800 mol/kmol.

The amount of the α-olefin is adjusted based on the desired density of the first ethylene polymer mixture and it, too, depends on the specific catalyst used. For many generally used Ziegler – Natta catalysts the molar ratio of the α-olefin to ethylene is forexample from 0 to 1000 mol/kmol, preferably from 0 to 800 mol/kmol and in particular from 0 to 700 mol/kmol.

The polymerisation of the second polymerisation step may also be conducted in gas phase in the same way as was discussed above for the first polymerisation step. Preferably the second polymerisation step is conducted in slurry phase as described above.

It is thus preferred to conduct the second polymerisation step for producing the first ethylene polymer mixture (PEM1) having MFR_2 of from 150 to 800 g/10 min , in slurry polymerisation. The molar ratio of hydrogen to ethylene is suitably from 250 to 1000 mol/kmol, preferably from 250 to 800 mol/kmol and in particular from 300 to 700 mol/kmol in the second polymerisation step.

Further, suitably the polymerisation is conducted at a temperature exceeding the critical temperature of the fluid mixture and pressure exceeding the critical pressure of the fluid mixture.

According to the present invention an α-olefin may optionally be present in the first polymerisation step and in the second polymerisation step. The density of the first ethylene homo- or copolymer is controlled by the molar ratio of the α-olefin to ethylene in the first polymerisation step and the density of the first ethylene polymer mixture is controlled by the molar ratio of the α-olefin to ethylene in the second polymerisation step. The molar ratio of the α-olefin to ethylene may then preferably be for example from 50 to 1000 mol/kmol, and preferably from 100 to 600 mol/kmol in the second polymerisation step.

The α-olefin used in the second polymerisation step may be the same or different as used in the first polymerisation step.

The polymerisation rate in the second polymerisation step is suitably controlled to achieve the desired amount of the second ethylene homo- or copolymer in the second ethylene polymer mixture. Preferably the second ethylene polymer mixture contains from 20 to 45 % by weight, preferably 25 to 40 % by weight, further preferred > 27 to < 40 % by weight of the second ethylene homo- or copolymer. The polymerisation rate is suitably controlled by adjusting the ethylene concentration in the second polymerisation step. When the second polymerisation step is conducted as slurry polymerisation in the loop reactor the mole fraction of ethylene in the reaction mixture is suitably from 2 to 10 % by mole and preferably from 3 to 8 % by mole.

As indicated above the melt flow rate MFR_2 of the first ethylene homo- or copolymer (PE1) is in the range 10 to < 150 g/10 min and and MFR_2 (PE1) < MFR_2(PEM1). I.e. the MFR_2 of the polymer produced in the first reactor is lower than the polymer mixture produced in the second polymerisation reactor.

Third Polymerisation Step

In the third polymerisation step the second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture (PEM1) and the third ethylene copolymer (PE3) is formed.

Into the third polymerisation step are introduced ethylene, at least one α-olefin having 4 to 10 carbon atoms, hydrogen and optionally an inert diluent. The polymerisation in third polymerisation step is conducted at a temperature within the range of from 50 to 100 °C, preferably from 60 to 100 °C and in particular from 70 to 95 °C. The pressure in the third polymerisation step is for example from 1 to 300 bar, preferably from 5 to 100 bar.

The polymerisation in the third polymerisation step may be conducted in slurry. The polymerisation may then be conducted along the lines as was discussed above for the first and second polymerisation steps.

The amount of hydrogen in the third polymerisation step is adjusted for achieving the desired melt flow rate of the second ethylene polymer mixture. The molar ratio of hydrogen to ethylene depends on the specific catalyst used. For many generally used Ziegler – Natta catalysts the molar ratio of hydrogen to ethylene is for example from 0 to 50 mol/kmol, preferably from 3 to 35 mol/kmol.

Furthermore, the amount of α-olefin having from 4 to 10 carbon atoms is adjusted to reach the targeted density. The ratio of the α-olefin (sum of α-olefins) to ethylene depends on the type of the catalyst and the type of the α-olefin. The ratio is typically from 100 to 1000 mol/kmol, preferably from > 100 to 500 mol/kmol. If more than one α-olefin is used the ratio of the α-olefin to ethylene is the ratio of the sum of all the α-olefins to ethylene.

The α-olefin used in the third polymerisation step may be the same or different as used in the previous polymerisation steps. The α-olefin is preferably an α-olefin of 4 to 8 carbon atoms or mixtures thereof. In particular 1-butene, 1-hexene and 1-octene and their mixtures are the preferred α-olefins.

Alternatively, the polymerisation in the third polymerisation step may be, and preferably is, conducted in gas phase. In gas phase polymerisation using a Ziegler – Natta catalyst hydrogen is typically added in such amount that the ratio of hydrogen to ethylene is for example from 3 to 100 mol/kmol, preferably from 4 to 50 mol/kmol for obtaining the desired melt index of the second ethylene polymer mixture. The amount of α-olefin having from 4 to 10 carbon atoms is adjusted to reach the targeted density of the second ethylene polymer mixture. The ratio of the α-olefin to ethylene is typically from 100 to 1000 mol/kmol, preferably from > 1000 to 500 mol/kmol. If more than one α-olefin is used the ratio of the α-olefin to ethylene is the ratio of the sum of all the α-olefins to ethylene.

The gas phase reactor preferably is a vertical fluidised bed reactor. There the polymer particles formed in the polymerisation are suspended in upwards moving gas. The gas is introduced into the bottom part of the reactor. The upwards moving gas passes the fluidised bed wherein a part of the gas reacts in the presence of the catalyst and the unreacted gas is withdrawn from the top of the reactor. The gas is then compressed and cooled to remove the heat of polymerisation. To increase the cooling capacity it is sometimes desired to cool the recycle gas to a temperature where a part of the gas condenses. After cooling the recycle gas is reintroduced into the bottom of the reactor. Fluidised bed polymerisation reactors are disclosed, among others, in US-A-4994534, US-A-4588790, EP-A-699213, EP-A-628343, FI-A-921632, FI-A-935856, US-A-4877587, FI-A-933073 and EP-A-75049.

When the second polymerisation step is conducted in slurry and the third polymerisation step is conducted in gas phase, the polymer is suitably transferred from the second polymerisation step into the third polymerisation step as described in EP-A-1415999. The procedure described in paragraphs [0037] to [0048] of EP-A-1415999 provides an economical and effective method for product transfer.

The polymerisation rate in the third polymerisation step is suitably controlled to achieve the desired amount of the third ethylene copolymer in the second ethylene polymer mixture. Preferably the second ethylene polymer mixture contains from 30 to 55 % by weight, preferably 35 to 50 % by weight by weight of the third ethylene copolymer. The polymerisation rate is suitably controlled by adjusting the ethylene concentration in the third polymerisation step.

When the third polymerisation step is conducted in gas phase the mole fraction of ethylene in the reactor gas may be suitably for example from 3 to 50 % by mole and preferably from 5 to 30 % by mole.

In addition to ethylene, comonomer and hydrogen the gas also comprises an inert gas. The inert gas can be any gas which is inert in the reaction conditions, such as a saturated hydrocarbon having from 1 to 5 carbon atoms, nitrogen or a mixture of the above-mentioned compounds. Suitable hydrocarbons having from 1 to 5 carbon atoms are methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane and mixtures thereof.

Values and/or properties reported for PEM2 may preferably be measured on pellets.

Post Reactor Treatment

When the polymer has been removed from the polymerisation reactor it is subjected to process steps for removing residual hydrocarbons from the polymer. Such processes are well known in the art and can include pressure reduction steps, purging steps, stripping steps, extraction steps and so on. Also combinations of different steps are possible.

According to one preferred process a part of the hydrocarbons is removed from the polymer powder by reducing the pressure. The powder is then contacted with steam at a temperature of from 90 to 110 °C for a period of from 10 minutes to 3 hours. Thereafter the powder is purged with inert gas, such as nitrogen, over a period of from 1 to 60 minutes at a temperature of from 20 to 80 °C.

According to another preferred process the polymer powder is subjected to a pressure reduction as described above. Thereafter it is purged with an inert gas, such as nitrogen, over a period of from 20 minutes to 5 hours at a temperature of from 50 to 90 °C. The inert gas may contain from 0.0001 to 5 %, preferably from 0.001 to 1 %, by weight of components for deactivating the catalyst contained in the polymer, such as steam.

The purging steps are preferably conducted continuously in a settled moving bed. The polymer moves downwards as a plug flow and the purge gas, which is introduced to the bottom of the bed, flows upwards.

Suitable processes for removing hydrocarbons from polymer are disclosed in WO-A-02/088194, EP-A-683176, EP-A-372239, EP-A-47077 and GB-A-1272778.

After the removal of residual hydrocarbons the polymer is preferably mixed with additives as it is well known in the art. Such additives include antioxidants, process stabilisers, neutralisers, lubricating agents, nucleating agents, pigments and so on.

The polymer particles are mixed with additives and extruded to pellets as it is known in the art. Preferably a counter-rotating twin screw extruder is used for the extrusion step. Such extruders are manufactured, for instance, by Kobe and Japan Steel Works. A suitable example of such extruders is disclosed in EP-A-1600276. Typically the specific energy input (SEI) is during the extrusion within the range of from 100 to 230 kWh/ton. The melt temperature is typically from 220 to 290 °C.

Preferred embodiments

In an embodiment the process according to the invention the α-olefin comonomer may be selected from the group consisting of α-olefins having from 4 to 10 carbon atoms and their mixtures, preferably from the group consisting of α-olefins having from 4 to 8 carbon atoms and their mixtures, further preferred from the group consisting of 1-butene, 1-hexene and 1-octene, further preferred wherein only ethylene is polymerized in the first and second polymerization steps and two comonomers are used in the third polymerization step, whereby the α-olefin comonomers used in the third polymerization step are 1-butene and/or 1-hexene.

In an embodiment the process according to the invention, the third polymerisation step may be conducted in gas phase, preferably in a gas phase fluidized bed reactor, further preferred connected in series.

In an embodiment the process according to the present invention at least one of the first and the second polymerisation step may be conducted as a slurry polymerisation in a loop reactor, preferably both the first and the second polymerisation steps are conducted as a slurry polymerisation in two loop reactors, preferably connected in series.

In an embodiment of the process according to the invention, diluent in the slurry polymerisation may comprise for example at least 90 % of hydrocarbons having from 3 to 5 carbon atoms.

In an embodiment of the process according to the invention, the second ethylene polymer mixture (PEM2) may comprise from 10 to 35 % by weight, preferably 13 to 26 % by weight, further preferred > 15 to < 25 % by weight of the first ethylene homo- or copolymer (PE1), from 20 to 45 % by weight, preferably 25 to 40 % by weight, further preferred > 27 to < 40 % by weight of the second ethylene homo- or copolymer (PE2) and from 30 to 55 % by weight, preferably 35 to 50 % by weight, of the third ethylene copolymer (PE3).

In an embodiment of the process according to the invention, the second ethylene polymer mixture may have a density of from 932 to 946 kg/m^3 and/or a melt flow rate MFR$_5$ of from 0.1 to 2 g/10 min, preferably from 0.5 to 1.8 g/10min.

In an embodiment of the process according to the invention, the second ethylene polymer mixture (PEM2) may have and a density of from 932 to 946 kg/m^3, the first ethylene homo- or copolymer (PE1) may have a density of from 940 to 980 kg/m^3 and/or a melt flow rate MFR$_2$ of from 12 to 75 g/10 min, preferably from 15 to 60 g/10 min and the first ethylene polymer mixture (PEM1) may have a density of from 940 to 980 kg/m^3 and/or a melt flow rate MFR$_2$ of from 85 to 165 g/10 min.

In an embodiment of the process according to the invention, the ratio MFR$_2$(PEM1) / MFR$_2$(PE1) may be between 1 and 8, preferably between 2 and 7.5.

The present invention also concerns a multimodal ethylene polymer film composition having density of from 930 to 955 kg/m^3 and/or a melt flow rate MFR$_5$ of from 0.3 to 5 g/10 min and produced according to the process described herein.

In an embodiment, multimodal ethylene- alpha-olefin copolymer film composition according to the invention may have a density of from 930 to 955 kg/m^3 and a melt flow rate MFR$_5$ of from 0.3 to 5 g/10 min and may comprise a first ethylene homo- or copolymer (PE1), a second ethylene homo- or copolymer (PE2) and a third ethylene copolymer (PE3), wherein the first ethylene homo- or copolymer (PE1) and the second ethylene homo- or copolymer (PE2) form a first ethylene polymer mixture (PEM1) and the first ethylene polymer mixture (PEM1) and the third ethylene copolymer (PE3) form the second ethylene polymer mixture (PEM2), and wherein

I. the first ethylene homo- or copolymer (PE1) may have a melt flow rate MFR$_2$ of from 10 to < 150 g/10 min and optionally a density of from 940 to 980 kg/m^3;
II. the first ethylene polymer mixture (PEM1) may have a melt flow rate MFR$_2$ of from 80 to 180 g/10 min and optionally a density of from 940 to 980 kg/m^3, wherein the MFR$_2$ of the first ethylene homo- or copolymer (PE1) may be lower than first ethylene polymer mixture (PEM1);

III. the second ethylene polymer mixture (PEM2) may have a density of from 930 to 955 kg/m^3 and a melt flow rate MFR$_5$ of from 0.3 to 5 g/10 min.

In an embodiment, a multimodal film composition according to the invention, the ratio MFR$_2$(PEM1) / MFR$_2$(PE1) may be between 1 and 8, preferably between 2 and 7.5.

Film

The film according to the present invention comprises the multimodal ethylene copolymer film composition, preferably a trimodal polyethylene film composition. In addition to the multimodal, preferably trimodal ethylene copolymer the film composition may also contain antioxidants, process stabilizers, slip agents, pigments, UV-stabilizers and other additives known in the art. Examples of stabilizers are hindered phenols, hindered amines, phosphates, phosphites and phosphonites. Examples of pigments are carbon black, ultramarine blue and titanium dioxide. Examples of other additives are e. g. clay, talc, calcium carbonate, calcium stearate, zinc stearate and antistatic additives like. The additives can be added as single components or as part of a masterbatch as is known in the art.

Suitable antioxidants and stabilizers are, for instance, 2,6-di-tert-butyl-p-cresol, tetrakis-[methylene-3-(3',5-di-tert-butyl-4'hydroxyphenyl)propionate]methane, octadecyl-3-3(3'5'-di-tert-butyl-4'-hydroxyphenyl)propionate, dilaurylthiodipropionate, distearylthiodipropionate, tris-(nonylphenyl)phosphate, distearyl-pentaerythritol-diphosphite and tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene-diphosphonite.

Some hindered phenols are sold under the trade names of Irganox 1076 and Irganox 1010 or commercially available blends thereof, like Irganox B561. Commercially available blends of antioxidants and process stabilizers are also available, such as Irganox B225 marketed by Ciba-Geigy.

Suitable acid scavengers are, for instance, metal stearates, such as calcium stearate and zinc stearate. They are used in amounts generally known in the art, typically from 300 ppm to 10000 ppm and preferably from 400 to 5000 ppm.

The polymer/composition of the invention can be provided in the form of powder or pellets, preferably pellets. Pellets are obtained by conventional extrusion, granulation or grinding techniques and are an ideal form of the polymer of the invention because they can be added directly to converting machinery. Pellets are distinguished from polymer powders where particle sizes are less than 1 mm. The use of pellets ensures that the composition of the invention is capable of being converted in a film, e.g. monolayer film, by the simple in line addition of the pellets to the converting machinery.

The multimodal ethylene polymer film compositions of the invention allow the formation of films having good mechanical properties. The composition can be extruded to films according to any method known in the art. The film preparation process steps of the invention are known and may be carried out in a film line in a manner known in the art, such as flat film extrusion or blown film extrusion. Well known film lines are commercially available, for example from Windmöller & Hölscher, Reifenhauser, Hosokawa Alpine etc.

Importantly, the ethylene polymer compositions of the invention have extraordinary processing properties. Multimodality, especially trimodality, of the polyethylene film composition of the invention makes it very beneficial for making films. Benefits can be seen in excellent extrudability and especially in the clearly higher throughput in the film making machinery than corresponding film materials having the same level of density and MFR. The high throughput is not achieved at the expense of good mechanical properties. In the film making process the maximum output of the film composition of the invention with 40 µm film is at least 15 % higher, preferably at least 20 % higher, more preferably at least 25 % higher, even more than 30 % higher than with commercial film composition having corresponding MFR and density as composition of the invention.

Thus, the multimodal film composition of the invention is very attractive in film making point of view.

The films of the invention are preferably monolayer films or the polymer composition of the invention is used to form a layer within a multilayer film. Any film of the invention may have a thickness of 3 to 1000 µm, preferably 5 to 500 µm, more preferably 10 to 250 µm, still more preferably 10 to 150 µm, such as e.g. 10 to 100 µm, or even 10 to 60 µm. Selected thickness is dependent on the needs of the desired end application.

The compositions produced according to the process of the present invention are suitable for making blown films. The films of the invention can be manufactured using simple in line addition of the polymer pellets to an extruder. For film formation using a polymer mixture it is important that the different polymer components be intimately mixed prior to extrusion and blowing of the film as otherwise there is a risk of inhomogeneity, e.g. gels, appearing in the film. Thus, it is especially preferred to thoroughly blend the components, for example using a twin screw extruder, preferably a counter- rotating extruder prior to extrusion and film blowing.

Sufficient homogeneity can also be obtained by selecting the screw design for the film extruder such that it is designed for good mixing and homogenizing. The film of the invention is a blown film. Blown films are typically produced by extrusion through an annular die, blowing into a tubular film by forming a bubble which is collapsed between nip rollers after solidification. This film can then be slit, cut or converted (e.g. gusseted) as desired. Conventional film production techniques may be used in this regard. Typically the composition will be extruded at a temperature in the range 160°C to 240°C, and cooled by blowing gas (generally air) at a temperature of 10 to 50°C to provide a frost line height of 1 or 2 to 8 times the diameter of the die. The blow up ratio (BUR) should generally be in the range 1.5 to 4, e.g. 2 to 4, preferably 2.5 to 3.

The films of the invention exhibit high dart impact strengths and tear strengths, especially in the machine direction. In the passages which follow, certain parameters are given based on a specific film thickness. This is because variations in thickness of the film cause a change to the size of the parameter in question so to obtain a quantitative value, a specific film thickness is quoted. This does not mean that the invention does not cover other film thicknesses rather it means that when formulated at a given thickness, the film should have the given parameter value.

Thus, for a 40 µm film manufactured as described below and at maximum output, Impact resistance on film (DDI) (ASTM D1709, method “A”) may be for example 200 g to 500 g and/or tensile modulus of for example between 400 MPa and 800 MPa, preferably > 500 MPa and < 700 MPa in MD (ISO 527-3).

The present invention also concerns a process for producing a film, comprising the steps of

(i) copolymerising ethylene and an alpha-olefin comonomer in a first polymerisation step in the presence of a silica supported Ziegler-Natta polymerisation catalyst to produce a first ethylene homo- or copolymer (PE1) having a melt flow rate MFR_2 of from 10 to < 150 g/10 min and optionally a density of from 940 to 980 kg/m^3;

(ii) copolymerising ethylene and an alpha-olefin comonomer in a second polymerisation step in the presence of the first ethylene homo- or copolymer to produce a first ethylene polymer mixture (PEM1) comprising the first ethylene homo- or copolymer and a second ethylene homo- or copolymer, said first ethylene polymer mixture (PEM1) a melt flow rate MFR_2 of from 80 to

180 g/10 min and optionally a density of from 940 to 980 kg/m^3, and wherein the MFR$_2$ of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1) and

(iii) copolymerising ethylene and an alpha-olefin comonomer in a third polymerisation step in the presence of the first ethylene polymer mixture to produce a second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture and a third ethylene copolymer, said second ethylene polymer mixture (PEM2) having a density of from 930 to 955 kg/m^3 and a melt flow rate MFR$_5$ of from 0.3 to 5 g/10 min and

iv) pelletizing the second polymer mixture and
v) providing a film by blow moulding.

In an embodiment of process for producing a film according to the invention the α-olefin comonomer may be selected from the group consisting of α-olefins having from 4 to 10 carbon atoms and their mixtures, preferably from the group consisting of α-olefins having from 4 to 8 carbon atoms and their mixtures, further preferred from the group consisting of 1-butene, 1-hexene and 1-octene, further preferred wherein only ethylene is polymerized in the first and second polymerization steps and two comonomers are used in the third polymerization step, whereby the α-olefin comonomers used in the third polymerization step are 1-butene and/or 1-hexene.

The invention also concerns a film as described herein.

Examples

Methods

The following methods were used to measure the properties that are defined generally above and in examples below. Unless otherwise stated, the film samples used for the measurements and definitions were prepared as described under the heading “Film Sample Preparation”.

Melt Index (MI) or Melt Flow Rate (MFR)

The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the melt viscosity of the polymer. The MFR is determined at 190°C for PE. The load under which the melt flow rate is determined is usually indicated as a subscript, for instance MFR$_2$ is measured under 2.16 kg load, MFR$_5$ is measured under 5 kg load and MFR$_{21}$ is measured under 21.6 kg load. MFR values can be determined on samples as explained above or calculated, for example in a way well known in the art, from MFR values determined on samples as explained above, especially for example an MFR value for the second ethylene homo- or copolymer can be calculated based on a measured MFR value for the first ethylene homo- or copolymer, a measured MFR value for the first ethylene polymer mixture and the respective amounts of the first and second ethylene homo- or copolymers, since the MFR of the first ethylene polymer mixture results from the first and second ethylene homo- or copolymers.

Density

Density of the polymer was measured according to ISO 1183-2 / 1872-2B.

Co-monomer content and thickness

Co-monomer content can be determined according to any suitable method well known in the art to do so, such as for example NMR. Film thickness can be determined according to any suitable method well known in the art to do so, such as for example any suitable measuring device.

Impact resistance on film (DDI)

Impact resistance on film (DDI) was determined by Dart-drop (g/50%). Dart-drop was measured using ASTM D1709, method "A" (Alternative Testing Technique). A dart with a 38 mm diameter hemispherical head was dropped from a height of 0.66 m onto a film clamped over a hole. If the specimen failed, the weight of the dart was reduced and if it did not fail the weight was increased. At least 20 specimens were tested. One weight is used for each set and the weight is increased (or decreased) from set to set by uniform increments. The weight resulting in failure of 50% of the specimens was calculated and reported

Tear resistance (determined as Elmendorf tear (N))

The tear strength or tear resistance is measured using the ISO 6383/2 method. The force required to propagate tearing across a film specimen is measured using a pendulum device. The pendulum swings under gravity through an arc, tearing the specimen from a pre-cut slit. The specimen is fixed on one side by the pendulum and on the other side by a stationary clamp. The tear strength or tear resistance is the force required to tear the specimen. The relative tear resistance (N/mm) can be calculated by dividing the tear resistance by the thickness of the film. The films were produced as described below in the film preparation example. The tear strength or tear resistance is measured in machine direction (MD) and/or transverse direction (TD)

Tensile modulus (E-Mod (MPa) was measured in machine and/or transverse direction according to ISO 527-3 on film samples prepared as described under the Film Sample preparation with film thickness of 40 µm and at a cross head speed of 1 mm/min for the modulus.

Shear Thinning Index (SHI)

Rheological parameters such as Shear Thinning Index SHI and Viscosity were determined by using a Anton Paar Phisica MCR 300 Rheometer on compression moulded samples under nitrogen atmosphere at 190 °C using 25 mm diameter plates and plate and plate geometry with a 1.2 mm gap. The oscillatory shear experiments were done within the linear viscosity range of strain at frequencies from 0.05 to 300 rad/s (ISO 6721-1). Five measurement points per decade were made.

The values of storage modulus (G´), loss modulus (G´´) complex modulus (G*) and complex viscosity (η^*) were obtained as a function of frequency (ω). η_{100} is used as abbreviation for the complex viscosity at the frequency of 100 rad/s.

Shear thinning index (SHI), which correlates with MWD and is independent of Mw, was calculated according to Heino ("Rheological characterization of polyethylene fractions" Heino, E.L., Lehtinen, A., Tanner J., Seppälä, J., Neste Oy, Porvoo, Finland, Theor. Appl. Rheol., Proc. Int. Congr. Rheol, 11th (1992), 1, 360-362, and "The influence of molecular structure on some rheological properties of polyethylene", Heino, E.L., Borealis Polymers Oy, Porvoo, Finland, Annual Transactions of the Nordic Rheology Society, 1995).

SHI value is obtained by calculating the complex viscosities at given values of complex modulus and calculating the ratio of the two viscosities. For example, using the values of complex modulus of 5 kPa and 300 kPa, then $\eta^*(5\ \text{kPa})$ and $\eta^*(300\ \text{kPa})$ are obtained at a constant value of complex modulus of 5 kPa and 300 kPa, respectively. The shear thinning index $SHI_{5/300}$ is then defined as the ratio of the two viscosities $\eta^*(5\ \text{kPa})$ and $\eta^*(300\ \text{kPa})$, i.e. $\eta(5)/\eta(300)$.

The films were prepared as described below in the film preparation method A.

Inventive Examples IE1-IE4

A loop reactor having a volume of 50 dm^3 was operated at a temperature of 60 °C (for IE1 and IE2) or 70 °C (for IE3 and IE4) and a pressure of 56 bar (for IE1, IE2 and IE4) or 57 bar (for IE3). Into the reactor were fed ethylene, 1-butene, propane diluent and hydrogen so that the feed rate of ethylene was 2.0 kg/h (for IE1 and IE2)or 4.0 kg/h (for IE3 and IE4), of 1-butene 50 g/h, of hydrogen was 10 g/h (IE1 and IE2) or 2.0 g/h (for IE3 and IE4). Also a solid polymerization catalyst component produced as described above and in Example 1 of EP 1378528 was introduced into the reactor together with triethylaluminium cocatalyst so that the molar ratio of Al/Ti was about 15. The estimated production rate was for example about 2.5 kg/h.

A stream of slurry was continuously withdrawn and directed to a loop reactor having a volume of 150 dm^3 and which was operated at a temperature of 95 °C and a pressure of 54 bar (for IE1 and IE2) or 55 bar (for IE3 and IE4). Into the reactor were further fed additional ethylene, propane diluent and hydrogen so that the ethylene concentration in the fluid mixture was 3,5 % by mole, the hydrogen to ethylene ratio was as indicated in the table below (see 1. reactor) and the molar ratio of 1-butene to ethylene was as indicated in the table below (see 1. reactor).

A stream of slurry from the reactor was withdrawn intermittently and directed into a loop reactor having a volume of 350 dm^3 and which was operated at 95 °C temperature and 51 bar (for IE1 and IE2) or 53 bar (for IE3 and IE4) pressure. Into the reactor was further added a fresh propane, ethylene, and hydrogen so that the ethylene content in the reaction mixture was 2.9 mol-% and the molar ratio of hydrogen to ethylene was as indicated in the table below (see 2. reactor) and the molar ratio of 1-butene to ethylene was as indicated in the table below (see 2. reactor). The production rate was for example about 30 kg/h.

The slurry was withdrawn from the loop reactor intermittently and directed to a flash vessel operated at a temperature of 50 °C and a pressure of 3 bar. From there the polymer was directed to a fluidized bed gas phase reactor operated at a pressure of 20 bar and a temperature of 80 °C. Additional ethylene hexene and optionally 1-butene comonomer, nitrogen as inert gas and hydrogen were added so that the ratio of hydrogen to ethylene and the molar ratio of hexane and/or 1-butene to ethylene were as indicated in the table below (see 3. reactor). The polymer production rate in the gas phase reactor was for example about 40 kg/h.. The polymer properties are indicated in the table below. The production split (weight-% prepolymer/weight-% 1st step component/weight-% 2nd step component/weight-% 3rd step component) is also indicated in the table below.

In Table 1 there is a summary of polymerisation conditions and material properties.

Table 1

	IE1	IE2	IE3	IE4
Prepol				
C2 kg/h	4	4	2	2
C4 g/h	50	50	50	50
H2 g/h	9.9	9.9	2	2
1. reactor (loop)				
C2 mol%	3.6	3.5	3.5	3.3
H2/C2/mol/kmol	293	312	297	325
C4/C2 (mol7kmol)	4.5	5.0	6.6	6.7
MFR2/g/10min	22	43	22.1	21.2
Split, %	22.3	22.1	24	32
2 reactor (loop)				
C2 mol%	2.9	2.9	2.9	2.9
H2/C2/mol/kmol	565	574	436	467
C4/C2 ratio (mol/kmol)	3.1	3.0	7.2	8.4
PEM1				
MFR2/g/10min	113	158	109	130
Split, %	32.7	31.2	36.5	37.1
3.reactor (gas phase)				
H2/C2/mol/kmol	35	41	27	36
C4/C2/mol/kmol	0	0	0	49
C6/C2/mol/kmol	202	315	164	74
Split, %	42	45	40	40.4
PEM2 (pellet)				
MFR5/g/10min	0.9	1.4	0.9	1.2
Density/ kg(m3	941.2	935.4	944.8	944.2

Comparative Material CM 1

As comparative material 1 was used commercial linear low density polyethylene film grade Borshape® FX1001 having the density of 931 kg/m^3 and MFR$_5$ of 0.9 g/10 min. SHI(5/300)=55.

Film preparation Method A

Blown films were made in 7-layer Alpine line under the following conditions: Extruder temperature settings were for all extruders: 220-230-230-230-230-235-235 in all test points.

Further the following parameters were used: Blow Up Ratio (BUR) of 3.0; frost line height of 850mm, which is about 3 times of die diameter (300mm); and die gap of 1,5mm. Layered structure of the monolayer film produced from 7-layer Alpine line of 14/14/14/14/14/15/15.

Blow Up Ratio (BUR) is defined to be Diameter of the bubble / Diameter of the die (represents TD orientation).

BUR indicates the increase in the bubble diameter over the die diameter. A blow-up ratio greater than 1 indicates that the bubble has been blown to a diameter greater than that of the die orifice. Maximum output rate (kg/h) was tested for materials at 40 micron film thickness.

Maximum output was restricted by extruder melt pressure limits. Individual throughputs of the extruders were adjusted so that in total max output (each extruder at max melt pressure) was reached. The maximum melt pressure for the Alpine line is 600 bars

Film Sample preparation

The blown film is wound to form reels which are followed by film cutting into respective dimension for further mechanical testing.

The compositions of CMs and IEs were used in producing blown films as indicated above.

Results are shown in Table 2 below.

Table 2

	Output, kg/h	Melt pressures in extruders (min-max), bar	E-mod MD, MPa	DDI, F50, g	Relative Tear Resistance MD, N/mm
CM 1	207	580 - 589	496	268	32
IE 1	210	430-488	651	337	22
IE2	209	397-442	536	352	26
IE3	329	557-565	592	265	13
IE4	272	511-548	608	247	15

Lower melt pressure levels in the extruders and/or higher output at the Alpine 7-layer blown film lare found for the inventive examples in comparison with the comparative examples. Furthermore, stiffness is improved for the inventive examples as can be seen by the values for E-modulus. In addition, DDI and Tear MD may be similar or even improved for the inventive examples

Claims

1. A process for producing multimodal ethylene polymer film compositions comprising the steps of

(i) copolymerising ethylene and optionally an alpha-olefin comonomer in a first polymerisation step in the presence of a silica supported Ziegler-Natta polymerisation catalyst to produce a first ethylene homo- or copolymer (PE1) having a melt flow rate MFR_2 of from 10 to < 150 g/10 min;

(ii) copolymerising ethylene and optionally an alpha-olefin comonomer in a second polymerisation step in the presence of the first ethylene homo- or copolymer to produce a first ethylene polymer mixture (PEM1) comprising the first ethylene homo- or copolymer and a second ethylene homo- or copolymer, said first ethylene polymer mixture having a melt flow rate MFR_2 of from 80 to 180 g/10 min, and wherein the MFR_2 of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1) and the second ethylene homo- or copolymer (PE2) has a melt flow rate MFR_2 of from 150 to 800 g/10min and

(iii) copolymerising ethylene and at least one alpha-olefin comonomer in a third polymerisation step in the presence of the first ethylene polymer mixture to produce a second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture and a third ethylene copolymer (PE3), said second ethylene polymer mixture having a density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min.

2. The process according to claim 1 wherein the α-olefin comonomer is selected from the group consisting of α-olefins having from 4 to 10 carbon atoms and their mixtures, preferably from the group consisting of α-olefins having from 4 to 8 carbon atoms and their mixtures, further preferred from the group consisting of 1-butene, 1-hexene and 1-octene, further preferred wherein only ethylene is polymerized in the first and second polymerization steps and two comonomers are used in the third polymerization step, whereby the α-olefin comonomers used in the third polymerization step are 1-butene and/or 1-hexene.

3. The process according to claim 1 or claim 2 wherein the third polymerisation step is conducted in gas phase, preferably in a gas phase fluidized bed reactor, further preferred connected in series.

4. The process according to any one of the preceding claims wherein at least one of the first and the second polymerisation step is conducted as a slurry polymerisation in a loop reactor,

preferably both the first and the second polymerisation steps are conducted as a slurry polymerisation in two loop reactors, preferably connected in series.

5. The process according to claim 4 wherein the diluent in the slurry polymerisation comprises at least 90 % of hydrocarbons having from 3 to 5 carbon atoms.

6. The process according to any one of the preceding claims wherein the second ethylene polymer mixture (PEM2) comprises from 10 to 35 % by weight, preferably 13 to 26 % by weight, further preferred > 15 to < 25 % by weight of the first ethylene homo- or copolymer (PE1), from 20 to 45 % by weight, preferably 25 to 40 % by weight, further preferred > 27 to < 40 % by weight of the second ethylene homo- or copolymer (PE2) and from 30 to 55 % by weight, preferably 35 to 50 % by weight, of the third ethylene copolymer (PE3).

7. The process according to any one of the preceding claims wherein second ethylene polymer mixture having a density of from 932 to 946 kg/m^3 and/or a melt flow rate MFR_5 of from 0.1 to 2 g/10 min, preferably from 0.5 to 1.8 g/10min.

8. The process according to any one of claims 1 to 7 wherein the second ethylene polymer mixture (PEM2) has and a density of from 932 to 946 kg/m^3, the first ethylene homo- or copolymer (PE1) has a density of from 940 to 980 kg/m^3 and a melt flow rate MFR_2 of from 12 to 75 g/10 min, preferably from 15 to 60 g/10 min and the first ethylene polymer mixture (PEM1) has a density of from 940 to 980 kg/m^3 and/or a melt flow rate MFR_2 of from 85 to 165 g/10 min.

9. The process according to any one of claims 1 to 8, wherein a ratio $MFR_2(PEM1) / MFR_2(PE1)$ is between 1 and 8, preferably between 2 and 7.5.

10. A multimodal ethylene polymer film composition having density of from 930 to 955 kg/m^3 and/or a melt flow rate MFR_5 of from 0.3 to 5 g/10 min and produced according to any of claim 1 to 9.

11. A multimodal ethylene- alpha-olefin copolymer film composition having density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min and comprising a first ethylene homo- or copolymer (PE1), a second ethylene homo- or copolymer (PE2) and a third ethylene copolymer (PE3), wherein the first ethylene homo- or copolymer (PE1) and the second ethylene homo- or copolymer (PE2) form a first ethylene polymer mixture (PEM1) and the first ethylene polymer mixture (PEM1) and the third ethylene copolymer (PE3) form the second ethylene polymer mixture (PEM2), and wherein

IV. the first ethylene homo- or copolymer (PE1) has a melt flow rate MFR_2 of from 10 to < 150 g/10 min;

V. the first ethylene polymer mixture (PEM1) has a melt flow rate MFR_2 of from 80 to 180 g/10 min, wherein the MFR_2 of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1);

VI. the second ethylene polymer mixture (PEM2) has a density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min.

12. A multimodal film composition according to claim 11, wherein a ratio $MFR_2(PEM1)$ / $MFR_2(PE1)$ is between 1 and 8, preferably between 2 and 7.5.

13. A process for producing a film, comprising the steps of

(i) copolymerising ethylene and an alpha-olefin comonomer in a first polymerisation step in the presence of a silica supported Ziegler-Natta polymerisation catalyst to produce a first ethylene homo- or copolymer (PE1) having a melt flow rate MFR_2 of from 10 to < 150 g/10 min;

(ii) copolymerising ethylene and an alpha-olefin comonomer in a second polymerisation step in the presence of the first ethylene homo- or copolymer to produce a first ethylene polymer mixture (PEM1) comprising the first ethylene homo- or copolymer and a second ethylene homo- or copolymer, said first ethylene polymer mixture (PEM1) having a melt flow rate MFR_2 of from 80 to 180 g/10 min, and wherein the MFR_2 of the first ethylene homo- or copolymer (PE1) is lower than first ethylene polymer mixture (PEM1) and

(iii) copolymerising ethylene and an alpha-olefin comonomer in a third polymerisation step in the presence of the first ethylene polymer mixture to produce a second ethylene polymer mixture (PEM2) comprising the first ethylene polymer mixture and a third ethylene copolymer, said second ethylene polymer mixture (PEM2) having a density of from 930 to 955 kg/m^3 and a melt flow rate MFR_5 of from 0.3 to 5 g/10 min and

vi) pelletizing the second polymer mixture and

vii) providing a film by blow moulding.

14. The process according to claim 13 wherein the α-olefin comonomer is selected from the group consisting of α-olefins having from 4 to 10 carbon atoms and their mixtures, preferably from the group consisting of α-olefins having from 4 to 8 carbon atoms and their mixtures, further preferred from the group consisting of 1-butene, 1-hexene and 1-octene, further preferred wherein only ethylene is polymerized in the first and second polymerization steps and

two comonomers are used in the third polymerization step, whereby the α-olefin comonomers used in the third polymerization step are 1-butene and/or 1-hexene.

15. A film comprising the multimodal film composition of claim 10 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/086917

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F210/16 C08J5/18 C08L23/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J C08F C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018/095788 A1 (BOREALIS AG [AT]) 31 May 2018 (2018-05-31) example 1 examples	1-15
A	WO 2018/095790 A1 (BOREALIS AG [AT]) 31 May 2018 (2018-05-31) the whole document	1-15
A	WO 2018/060029 A1 (BOREALIS AG [AT]) 5 April 2018 (2018-04-05) the whole document	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 9 March 2020	Date of mailing of the international search report 18/03/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Thomas, Dominik

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/086917

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