

PROCESS FOR PRODUCING PELLETS OF POLYOLEFINS, AND PELLETS SO PRODUCED

Field of the Invention

The present invention is directed to a process for producing pellets of polyolefins. Especially, the present invention is directed to a process for producing pellets from soft and sticky
5 polyolefins, like soft propylene copolymers or propylene based elastomers (POEs).

Background

Soft polyolefins, like soft propylene copolymers or propylene based elastomers (POEs), have attracted huge attention in the past due to their excellent combination of cost and performance.

For Example, copolymers of propylene with a comonomer selected from ethylene and alpha-
10 olefins having from 4 to 10 carbon atoms and containing from 7 to 20% by weight of comonomer and a content of xylene cold soluble (XCS) fraction of from 20 to 60% by weight have a unique combination of softness, retortability, impact strength and optical properties.

It is known that most of the plastic resins sold in the market today is in the form of pellets. Plastic resins are sold in the form of pellets to improve transportation, handling, safety and
15 end-user processability characteristics.

In the polyolefin production process, the polyolefin is therefore generally extruded and cut to pellets. During the extrusion process other ingredients like additives, fillers and/or pigments are usually added and mixed in to improve the polymer properties. In the extrusion stage the polyolefin is heated and melted. The melt is then pressed through a die plate, usually into a
20 water bath. The molten strands then solidify due to the cooling effect of the water. After the die plate there is usually a rotating cutter which cuts the solidified strands to pellets. The pellets are then dried and transported to a silo for storage and packaging.

A frequently used step in drying the pellets is to pass the slurry containing water and pellets to a sieve. The water passes through the sieve while the pellets are trapped by it and are
25 conveyed to subsequent process steps.

However, if pellets from a soft polyolefin are produced, the pellets tend to adhere, for instance, to the walls of the process apparatus. Especially the pellets have a strong tendency of adhering to each other, for instance during the pelletization, transport or storage.

The size, shape and uniformity of the pellets are important characteristics to be met during the
30 production. The pelletizing step is also important from the operational standpoint. Any malfunction of the pelletizer can result in process shutdown and manufacturing halt with

serious financial consequences, especially for large extrusion lines. As a consequence, the pelletization step is recognized to be an important step both in the production line of any polymer production plant and on a compounding line during a further extrusion step.

5 Efficient and satisfying pelletization is difficult to be achieved particularly when the final polymer exhibits softness and tackiness properties leading to poor flowability and agglomeration of the pellets. Formation of miscuts, multiples (such as doubles) in large amount in the pelletization process is a clear sign of reduced pellet quality.

Various systems have been proposed and are used to avoid or limit the tendency to pellets agglomeration, but fundamentally they can be subdivided in two methods:

10 1) introduction of a modifier within the polymer itself leading to a decrease of the tackiness by means of increasing of the crystallization kinetic or by a surface migration of the modifier;

2) surface treatment of the pellets with fine powdery materials (both organic or inorganic like for instance HDPE, talc, silica), or liquid compounds available for this purpose on the market under different trademarks.

15 For example, US 2004/0209082 discloses a process for coating tacky or soft polymer pellets. The pellets were coated with fine powder selected from talc, magnesium silicate, calcium silicate, calcium carbonate, cellulose, wood fibre, polyolefin wax and silica. The powders were used together with a binder. Such coating agents and binders will end up in the final articles produced from these polymers, deteriorating their mechanical and optical performance.

20 EP 3230348 discloses a process for extruding and pelletizing a propylene copolymer having a content of comonomer from 5 to 40% by mole, a melt flow rate MFR_2 measured at 230 °C under a load of 2.16 kg of from 0.5 to 15 g/10 min and a content of xylene cold soluble (XCS) fraction of from 20 to 60% by weight, said process comprising extruding the propylene copolymer through a die plate into an underwater pelletizer and cutting strands of the
25 propylene copolymer into pellets in the underwater pelletizer, wherein the ratio of the mass flow rate of the propylene copolymer to the mass flow rate of the cooling water is from 0.020 to 0.060; and the propylene copolymer comprises a polymeric nucleating agent, whereby propylene copolymer and the polymeric nucleating agent yield a composition, and whereby the composition has a crystallization temperature T_c as determined by DSC with a scan rate
30 of 10 °C/min in the range of 114 to 126 °C. This approach has been found to have limitations at low crystallinity, and it necessarily reduces softness of the product.

EP 3498799 suggests to use a polypropylene copolymer wax as a modifier for soft plastomers and therefore discloses a polyolefin composition comprising

- a) 60 to 99 wt.-% of a polyethylene plastomer, which is a copolymer of ethylene and one or more C3-C12 α -olefins, having a density of less than 904 kg/m³; and
- b) 1 to 40 wt.-% of a polypropylene copolymer wax having a melt flow rate (MFR) at 230 °C/2.16 kg of more than 400 g/10min.
- 5 Waxes, as proposed in this approach, are known to migrate to the surface of the final products, thus deteriorating application properties.

The use of organometallic surfactants to minimize the pellet agglomeration problem is also known in the art. However, when these surfactants are used with the effective amount, it often

10 results in severe foaming problems, and the foam may overflow from the water tank to the floor and thereby cause messy operation and unsafe working conditions. The combination of a defoamer, such as FOAMTROL® and an organometallic surfactant, such as zinc stearate has been used with some success. However, this combination has the drawback of the potential carcinogenic nature of FOAMTROL®.

- 15 US 4359544 proposes the use of a nucleating agent package as pelletizing aid, which package is a mixture of HDPE and stearamide. However, both HDPE and stearamide do not disperse well in water, and thus do not work well in a water bath as pelletizing aids.

Thus, although several options have already been suggested, there still remains a need for a simple and economical process which overcomes the problem of agglomeration of pellets.

- 20 Carboxylic acid metal salts of tetrahydrophthalic anhydride are known to be effective beta-nucleating agents for polypropylene.

For example, WO 2013097647 proposes such metal salts for increasing the heat resistance, toughness, and stiffness of polypropylene compositions. WO 2013097647 is silent about soft polyolefins and the problems related to the softness of the polyolefins in pelletization.

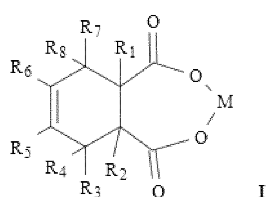
- 25 Also, CN102181092 suggests to use these metal salts in polypropylene to achieve beta-nucleation and thus improve properties like impact strength and thermal deformation temperature. According to CN102181092 such modified polypropylene can be used for preparing pipes.

- Again, soft polyolefins and the problems related to the softness of the polyolefins in pelletization are not mentioned.
- 30

Summary of the invention

The present invention is therefore directed to a process for producing pellets of polyolefins, the process comprising the steps of

- i-a) introducing a soft polyolefin, the soft polyolefin being characterized by
- a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa and
- 5 a content of chain units derived from propylene, determined with $^{13}\text{C}\{^1\text{H}\}$ NMR as described in the experimental part, of more than 50 wt.-%, based on the total weight of the soft polyolefin;
- i-b) 10 to 1000 ppm, based on the total weight of the polyolefin, of a pelletization agent of formula (I)



- 10 wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 are independently selected from H, C_1 - C_9 alkyl, hydroxyl, phenyl, C_1 - C_{18} - alkylphenyl and halogen, M is metal cation selected from Mg, Ca, Zn, Sr, Ba, La and Eu and

- i-c) 500 to 10000 ppm in total, based on the total weight of the polyolefin of one or more additives selected from the group consisting of antioxidants and process stabilisers, UV-
- 15 stabilisers, heat stabilisers, slip agents, antiblocking agents, acid scavengers, metal deactivators, antimicrobial agents antistatic agents and pigments

into a type of continuous mixer,

- ii) melting the polyolefin containing the pelletization agent i-b) and additives i-c) forming a molten polyolefin composition,
- 20 iii) extruding the molten polyolefin composition through a die plate having a multitude of holes into a pellet water bath in a pelletizer thereby producing strands of the polyolefin composition and solidifying the strands,
- iv) cutting the strands of the polyolefin composition in the pelletizer into pellets, and
- v) drying the pellets.

The process of the present invention is particularly efficient in causing a significant reduction of the tackiness of polyolefin pellets obtained from extrusion and pelletization of soft polyolefins.

Definitions

- 5 Where the term "comprising" is used in the present description and claims, it does not exclude other non-specified elements of major or minor functional importance. For the purposes of the present invention, the term "consisting of" is considered to be a preferred embodiment of the term "comprising of". If hereinafter a group is defined to comprise at least a certain number of embodiments, this is also to be understood to disclose a group, which preferably consists only
10 of these embodiments.

Whenever the terms "including" or "having" are used, these terms are meant to be equivalent to "comprising" as defined above.

- Where an indefinite or definite article is used when referring to a singular noun, e.g. "a", "an"
15 or "the", this includes a plural of that noun unless something else is specifically stated.

The term "soft polyolefin" applies to polyolefins having a low flexural modulus. Thus, in the present invention soft polyolefins are polyolefins having a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa.

- 20 Said soft polyolefins are predominantly based on polypropylene, i.e. have a content of chain units derived from propylene of more than 50 wt.-%.

Preferably, such soft polyolefins are furthermore characterized by a high content of soluble fraction, determined according to the CRYSTEX QC method, being in the range of 20 to 80 wt.-%.

- 25 It is also understood within the meaning of this disclosure that the below described embodiments may be combined.

Detailed description

Ad soft polyolefins:

The process of the present invention is related to the pelletization soft polyolefins.

- 30 All the types of polyolefins, which are predominantly based on polypropylene, showing high softness and tackiness may be suitably treated according to the process of this invention.

As mentioned above, such soft polyolefins are in general characterized by a low flexural modulus.

Thus, polyolefins, which are predominantly based on polypropylene and which may be suitably treated according to the process of this invention have a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa, preferably 15 to 500 MPa, more preferably 20 to 400 MPa and even more preferably 50 to 350 MPa.

The term polyolefins as used herein, unless otherwise specified, includes polypropylene polymers like homopolymers, copolymers, terpolymers and all other known combinations or forms of polymeric materials. The homopolymers generally have less crystallization problems, and accordingly their respective pellets show minor tendency to agglomerate each other.

Therefore, the present invention is preferably suitable for polyolefins, which are predominantly based on polypropylene, being copolymers or terpolymers, more preferably copolymers.

Such copolymers comprise an olefin monomer and at least one comonomer.

The olefin monomer can be any alpha-olefin monomer. Preferably, the olefin monomer is an alpha-olefin having from 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms. Especially preferably the olefin monomer is ethylene, propylene or 1-butene and in particular ethylene or propylene.

The olefin copolymer comprises more than 50 wt.-% of chain units derived from the propylene monomer, based on all the monomeric units in the copolymer. Preferably, the olefin copolymer comprises from 70 to 95 wt.-%, more preferably from 80 to 95 wt.-% of chain units derived from the propylene monomer, based on all the monomeric units in the copolymer.

The comonomer can be an alpha-olefin comonomer. The comonomer is preferably an alpha-olefin having from 2 to 10 carbon atoms and which is different from the olefin monomer. More preferably, the comonomer is an alpha-olefin having from 2 to 8 carbon atoms and which is different from the olefin monomer.

The alpha-olefin comonomer is especially preferably selected from the group consisting of ethylene, 1-butene, 1-hexene, 1-octene and mixtures thereof. More preferably, the comonomer is ethylene, 1-butene or 1-hexene or mixtures thereof, most preferably ethylene and/or 1-butene.

The polyolefin, preferably the olefin copolymer can be produced in the presence of a polymerization catalyst in any suitable polymerization process, such as slurry, gas phase or solution polymerization or combinations thereof, like slurry-gas phase polymerization.

The polymerization for producing polyolefins, preferably olefin copolymers, is well known to the person skilled in the art, including the polymerization processes and the catalysts used in them. Especially, the person skilled in the art is capable of controlling the density or comonomer content of the polymer by suitable addition of the comonomer and the molecular weight or the melt index by suitable addition of hydrogen.

Polyolefins, which are advantageously pelletized according to the process of the present invention, are soft propylene copolymers, more preferably propylene-ethylene, propylene-1-butene and propylene-ethylene-1-butene copolymers.

It is preferred to produce the propylene copolymers by known processes, in a one stage or two stage polymerization process, comprising solution polymerization, slurry polymerization, gas phase polymerization or combinations therefrom, in the presence of suitable Ziegler-Natta or metallocene catalysts.

In case the propylene copolymer is produced in a solution polymerization process, the propylene copolymer is preferably a propylene based elastomer, having a density in the range of 850 to 890 kg/m³, preferably in the range of 860 to 890 kg/m³, determined according to ISO 1183.

The MFR₂ (ISO 1133) of the propylene based elastomer at 230 °C is preferably between 0.5 and 100 g/10min, more preferably between 0.8 and 50 g/10 min, such as 1.0 to 30 g/10min.

The melting points (measured with DSC according to ISO 11357-1) of suitable propylene based elastomers are typically below 100 °C, preferably below 90 °C and more preferably below 80 °C. A reasonable lower limit for the melting points of suitable propylene based elastomers may be 35 °C.

Such propylene based elastomers are copolymers of propylene and 1-butene and/or ethylene comonomer(s).

In general, the solution polymerization may be accomplished at conditions well known in the prior art for olefin solution polymerization reactions. Preferred polymerization temperatures are from 80 to 250 °C, more preferably from 100 to 200 °C. Preferred polymerization pressures are from atmospheric to 3000 atmospheres (100 kPa to 300 MPa), more preferably from 1 MPa to 10 MPa. Highly desirable, the reaction is conducted under continuous, solution polymerization conditions, that is, conditions wherein the monomer or monomers are continuously added to a reactor operating under solution polymerization conditions, and polymerized product is continuously or semi-continuously removed and recovered or forwarded to a second reactor.

Desirably, the polymerization mixture comprises an aliphatic or alicyclic liquid diluent. Examples of such aliphatic or alicyclic liquid diluents include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; and perfluorinated hydrocarbons, and the like. Small quantities of aromatic hydrocarbons such as toluene, ethylbenzene or xylene may be included as well, but are not preferred. Mixtures of the foregoing are also suitable. A preferred liquid diluent is a hydrogenated oligomeric aliphatic hydrocarbon mixture having a distillation, ASTM D 86, IBP of 118 °C, distillation, ASTM D 86, Dry Point of 137 °C, and Specific Gravity, ASTM D 1250 of 0.72 sold commercially under the trade designation Isopar™ E, available from ExxonMobil Corporation.

The use of molecular weight control agents or chain transfer agents in the present process is desired. Examples of such molecular weight control agents include hydrogen, trialkyl aluminum compounds, or other known chain transfer agents. Hydrogen is a most preferred molecular weight control agent or chain transfer agent.

Such processes are disclosed, among others, in WO 2011/087729; WO 2011/087730; and WO 2011/087731.

Preferably, the propylene based polyolefins, preferably propylene copolymers are prepared in a single stage or multi-stage polymerization process including bulk slurry and gas phase polymerization steps. A preferred multistage process is a "loop-gas phase"- process, such as developed by Borealis (known as BORSTAR® technology) described e.g. in patent literature, such as in EP 1 681 315 A1 or WO 2013/092620 A1.

A further suitable slurry-gas phase process is the Spheripol® process of LyondellBasell.

A further suitably process for producing propylene based polyolefins, preferably olefin copolymers is LyondellBasell's proprietary Catalloy process, where the polymerization takes place in the presence of a specific Ziegler-Natta catalyst in a sequence of up to four sequential gas phase reactors.

More preferably the propylene based polyolefins, preferably propylene copolymers, being suitable for being used in the present invention, are produced in an at least 2-stage polymerization process, preferably in a process including at least one slurry polymerization step with at least one subsequent gas phase polymerization step, optionally followed by a second gas phase polymerization step and optionally a third gas phase polymerization step.

The polymerization conditions in the sequential polymerization of the propylene based polyolefins, preferably olefin copolymers, are nothing specific and well known to the skilled person. Typically a first (F1) is produced in a slurry reactor and a second fraction (F2) is produced in a gas phase reactor in the presence of the first fraction (F1), optionally followed
5 by a polymerization step in a second or even third gas phase reactor.

As mentioned above, such a process is known as BORSTAR® technology.

It is well known that prior to the main polymerization a prepolymerization may take place.

Regarding the prepolymerization, reference is made to WO2015/011134.

In case a prepolymerization step is performed, all of the catalyst mixture is introduced to the prepolymerization step.
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The temperature in the slurry polymerization is typically from 50 to 110 °C, preferably from 60 to 100 °C and in particular from 65 to 95 °C. The pressure is from 1 to 150 bar, preferably from 10 to 100 bar.

The slurry polymerization may be conducted in any known reactor used for slurry
15 polymerization. Such reactors include a continuous stirred tank reactor and a loop reactor. 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.

The residence time can vary in the reactor zones identified above. In one embodiment, the residence time in the slurry reactor, for example a loop reactor, is in the range of from 0.5 to
20 5 hours, for example 0.5 to 2 hours, while the residence time in the gas phase reactor generally will be in the range from 1 to 8 hours, like from 1.5 to 4 hours.

Into the slurry polymerization stage other components may also be introduced as it is known in the art. Thus, hydrogen is added to control the molecular weight of the polymer.

The slurry polymerization stage is followed by the gas phase polymerization stage in which a
25 fraction (F2) is produced. It is preferred to conduct the slurry directly into the gas phase polymerization zone without a flash step between the stages. This kind of direct feed is described in EP-A-887379, EP-A-887380, EP-A-887381 and EP-A-991684.

That is, the reaction product of the slurry phase polymerization, i.e. the first fraction (F1), which preferably is carried out in a loop reactor, is then transferred to the subsequent gas phase
30 reactor in which the second fraction (F2) is produced.

The polymerization in gas phase may be conducted in fluidized bed reactors, in fast fluidized bed reactors or in settled bed reactors or in any combination of these. When a combination of reactors is used then the polymer is transferred from one polymerization reactor to another.

Typically the gas phase reactor is operated at a temperature within the range of from 50 to 100 °C, preferably from 65 to 95 °C. The pressure is suitably from 10 to 40 bar, preferably from 15 to 30 bar.

One specific class of propylene based polyolefins, which is especially suitable for the process according to the present invention are random-heterophasic propylene-ethylene copolymers (RAHECO).

10 Such a random-heterophasic propylene-ethylene copolymer (RAHECO) comprises:

- a) a crystalline matrix (M) being a propylene-ethylene random copolymer; and
- b) an amorphous propylene-ethylene elastomer (E).

They can be produced in an at least 2-stage polymerization process, preferably a 3-stage polymerization process, in the presence of a catalyst.

15 The polymerization catalyst may be any suitable polymerization catalyst known in the art, which is capable of producing polypropylene and which has the desired stereoselectivity. Thus, the catalyst can be a metallocene catalyst, such as those disclosed in EP-A-629631, EP-A-629632, WO-A-00/26266, WO-A-02/002576, WO-A-02/002575, WO-A-99/12943, WO-A-98/40331, EP-A-776913, EP-A-1074557 and WO-A-99/42497 or a Ziegler-Natta catalyst,
20 such as those disclosed in WO-A-2003/000757, WO-A-2003/000754, WO-A-2004/029112, WO-A-2007/137853, WO-A-2012/007430, EP-A-2610271, EP-A-261027 and EP-A-2610272.

Preferably, the catalyst is a Ziegler-Natta catalyst comprising a solid component, the solid component comprising magnesium, titanium, halogen and an internal electron donor; an aluminium alkyl compound; and an external electron donor.

25 The aluminium alkyl compound is preferably a trialkylaluminium, and is more preferably selected from the group consisting of triethylaluminium, tri-isobutylaluminium, trimethylaluminium, tri-n-hexylaluminium and tri-n-octylaluminium and their mixtures.

The external electron donor is preferably a silicon ether and is more preferably selected from the group consisting of dicyclopentylmethoxysilane, cyclohexylmethyldimethoxysilane and
30 diethylaminotriethoxysilane.

Suitable RAHECOs may be characterized by the following properties:

The random-heterophasic propylene-ethylene copolymer (RAHECO) has a melt flow rate (MFR₂), determined according to ISO 1133 at 230 °C and 2.16 kg, in the range from 0.1 to 100 g/10 min, more preferably in the range from 0.3 to 50.0 g/10 min, even more preferably in the range from 0.5 to 20.0 g/10 min and most preferably in the range of 0.8 to 10.0 g/ 10 min.

- 5 The random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has a melting temperature (T_m), determined by differential scanning calorimetry (DSC), in the range from 130 °C to 160 °C, more preferably of from 140 °C to 157 °C and most preferably of from 145 °C to 155 °C.

- 10 The random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has an ethylene content (C₂(total)), determined by FT-IR spectroscopy calibrated by quantitative ¹³C-NMR spectroscopy in the CRYSTEX QC method, in the range from 3.0 to 25.0 wt.-%, more preferably in the range from 5.0 to 20.0 wt.-%, most preferably in the range from 8.0 to 15.0 wt.-%.

- 15 The polymeric part of the random-heterophasic propylene-ethylene copolymer (RAHECO) may be characterized according to the CRYSTEX QC method using trichlorobenzene (TCB) as a solvent. This method is described below in the determination methods section. The crystalline fraction (CF) contains for the most part the matrix phase and only a small part of the elastomeric phase and the soluble fraction (SF) contains for the most part the elastomeric phase and only a small part of the matrix phase. In some cases, this method results in more
20 useful data, since the crystalline fraction (CF) and the soluble fraction (SF) more accurately correspond to the matrix and elastomeric phases respectively. Due to the differences in the separation methods of xylene extraction and CRYSTEX QC method the properties of XCS/XCI fractions on the one hand and crystalline/soluble (CF/SF) fractions on the other hand are not exactly the same, meaning that the amounts of matrix phase and elastomeric phase can differ
25 as well as the properties.

The random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has a soluble fraction (SF) content, based on the total amount of the RAHECO, determined according to CRYSTEX QC analysis, in the range from 20 to 80 wt.-%, more preferably in the range from 25 to 60 wt.-%, most preferably in the range from 30 to 50 wt.-%.

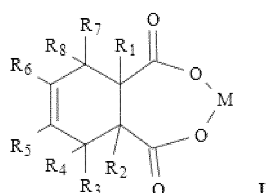
- 30 The random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has an ethylene content of the soluble fraction (C₂(SF)), according to CRYSTEX QC analysis, determined by FT-IR spectroscopy calibrated by quantitative ¹³C-NMR spectroscopy in the CRYSTEX QC method, in the range from 20 to 80 wt.-%, more preferably in the range from 23 to 60 wt.-%, most preferably in the range from 25 to 50 wt.-%.

The random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has an intrinsic viscosity, determined according to DIN ISO 1628/1, of the soluble fraction (iV(SF)), according to CRYSTEX QC analysis, in the range from 1.20 to 6.0 dL/g, more preferably in the range from 1.50 to 5.0 dL/g, most preferably in the range from 2.0 to 4.0 dL/g.

- 5 Further, the random-heterophasic propylene-ethylene copolymer (RAHECO) preferably has a flexural modulus of from 130 MPa to 500 MPa, more preferably of from 150 MPa to 450 MPa and most preferably of from 175 MPa to 400 MPa, determined according to ISO 178 on injection moulded test specimens.

Ad pelletizing agent

- 10 The process according to the present invention uses a pelletization agent of formula (I)



wherein R1, R2, R3, R4, R5, R6, R7, R8 are independently selected from H, C₁-C₉-alkyl, hydroxyl, phenyl, C₁-C₁₈-alkylphenyl and halogen, M is metal cation selected from Mg, Ca, Zn, Sr, Ba, La and Eu.

- 15 Suitable C₁-C₉-alkyl groups are linear or branched alkyl groups like methyl, ethyl, n-butyl, i-butyl, preferably linear or branched C₁-C₄-alkyl, more preferably methyl and ethyl.

Preferred C₁-C₁₈-alkylphenyl groups are C₁-C₁₀-alkyl phenyl groups, more preferably C₁-C₄-alkylphenyl groups.

Suitable halogen substituents are chloro, fluoro or bromo, preferably chloro.

- 20 Preferably, R1 to R8 are independently selected from the group consisting of hydrogen and C₁-C₄-alkyl, more preferably from hydrogen, methyl and ethyl.

Preferably, M is a metal cation selected from Mg, Ca, Zn, La, more preferably M is Ca or Zn, even more preferred M is Ca.

- 25 It is particularly preferred that each of R1 to R8 are hydrogen, i.e. that the dicarboxylic acid is 4-cyclohexene-1,2-dicarboxylic acid, with the most preferred dicarboxylic acid being cis-4-cyclohexene-1,2-dicarboxylic acid.

Such dicarboxylic metal salts are commercially available or can be produced as described for example in CN102181092.

The pelletization agent of formula (I) is added to the polyolefin in an amount of 10 to 1000 ppm, based on the total weight of the polyolefin.

- 5 Preferably the pelletization agent of formula (I) is added in an amount of 15 to 500 ppm, more preferably in an amount of 20 to 100 ppm and most preferably in an amount of 25 to 80 ppm.

Further additives

According to the present invention further, usual additives are added.

- 10 Such additives are selected from the group consisting of antioxidants and process stabilisers, UV-stabilisers, heat stabilisers, slip agents, antiblocking agents, acid scavengers, metal deactivators, antimicrobial agents, antistatic agents and pigments.

Preferably at least one or more antioxidants and an acid scavenger are added.

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

- 15 Such additives are commercially available and for example described in "Plastic Additives Handbook", 6th edition 2009 of Hans Zweifel (pages 1141 to 1190).

Usually, these additives are added in quantities of 100 to 2000 ppm for each single component.

- 20 The total amount of additives, which is added to the polyolefin, is in the range of 500 to 1000 ppm, based on the total weight of the polyolefin.

Process

The process of the present invention comprising several steps.

1st step:

- 25 i) introducing a polyolefin, pelletizing agent, as described above, and one or more additives, as described above into a type of continuous mixer.

Thus, in step i) the polyolefin, which has been removed from the polymerization reactor in powder form, the pelletizing agent and the further additives are introduced into a type of continuous mixer, preferably into an extruder.

The polyolefin powder is usually subjected to process steps for removing residual hydrocarbons from the polyolefin before the extrusion step. 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. 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.

Typically, the pelletizing agent and the additives are introduced into the feed port of the extruder together with the polyolefin.

The extrusion is preferably conducted in a twin screw extruder. Suitable twin screw extruders are co-rotating twin screw extruders and counter-rotating twin screw extruders. Co-rotating twin screw extruders are manufactured, among others, by Coperion, KraussMaffei Berstorff and Japan Steel Works. Counter-rotating extruders are manufactured, among others, by Farrel, Kobe Industries and Japan Steel Works. The twin screw extruders and their operation are within the skill of the person skilled in the art.

The extruder typically comprises one or more feed ports into which the polyolefin is introduced. Downstream of the feed port there is a melting zone and downstream of the melting zone one or more mixing zones. At the end of the extruder there is a die plate having a plurality of openings through which the molten plastic is extruded. The extruder may further comprise a screen pack with one or more screens for removing impurities or inhomogeneities. It may further comprise one or more gear pumps for generating sufficient pressure.

Suitable other types of continuous mixers include single-screw co-kneaders of the Buss type, chamber kneaders like the Farrell type or combinations of single-screw extruders and/or melt pumps with static mixers, like those of the Sulzer type.

2nd step

ii) melting i-a) the polyolefin containing the pelletization agent i-b) and additives i-c) in the type of continuous mixer, preferably in the extruder forming a molten polyolefin composition.

For melting the polyolefin, the temperature in the type of continuous mixer, preferably in the extruder is typically adjusted to a range of from 150 to 300 °C, preferably from 170 to 290 °C.

As suitable extruder can have several temperature zones, the temperature can be different in the different zones, within the above described temperature range.

The melt temperature in the extruder at or close to the die plate is typically adjusted to a range of from 190 to 250 °C, preferably from 200 to 240 °C.

As it is known to the person skilled in the art the melt temperature is influenced by the specific energy input into the melt and can thus be controlled by adjusting, for instance, the throughput or the rotation speed of the screw.

3rd step and 4th step

- 5 iii) extruding the molten polyolefin composition through a die plate having a multitude of holes into a pellet water bath in a pelletizer thereby producing strands of the polyolefin composition and solidifying the strands.

iv) cutting the strands of the polyolefin composition in the pelletizer into pellets.

10 The pellets are formed by extruding the polymer melt through the holes in the die plate to strands. The strands pass through the die plate into a water bath in an underwater pelletizer. At or immediately after the die plate there is a set of rotating knives, which cut the strands to pellets. Water is continuously added to the bath and slurry comprising the water and the pellets is continuously withdrawn from the pelletizer.

15 The die plate has a multiple of openings through which the molten polymer flows into the pelletizer. The openings have typically a diameter of from 2.0 to 3.0 mm so that the flow velocity of the polymer melt through the openings is from about 0.7 to 2.0 m/s, preferably from 0.8 to 1.5 m/s, such as 0.9 to 1.4 m/s.

The temperature of the pellet water in the pelletizer is typically from 10 to 70 °C.

20 For pelletizing the propylene based polyolefin, preferably the random-heterophasic propylene-ethylene copolymer (RAHECO), the temperature of the pellet water in the pelletizer is preferably from 15 to 55 °C, more preferably from 20 to 50 °C, even more preferably from 25 to 40 °C.

The pressure is not critical and can be selected based on the needs, such as from 1 to 10 bar (absolute pressure).

25 The residence time of the pellets in the pelletizer and piping between the pelletizer and the dryer is preferably within the range of from 5 to 30 seconds, more preferably from 5 to 20 seconds and especially preferably from 7 to 15 seconds. When the residence time is within these limits it has been found that the number of agglomerations of pellets is reduced.

5th step

- 30 v) drying the pellets

The slurry, as described above, is then passed to a dryer where the pellets are separated from the water.

One suitable way of removing the pellets from the pellet water is by using a rotating / spinning separator.

- 5 Therein, the pellet slurry is put into a rotating motion. The liquid is pressed through a screen at the periphery of the rotating dryer while the pellets are trapped inside.

Any other suitable liquid/solid separators may be used.

- 10 Another suitable way of removing pellets from the pellet water is by using a sieve. In a sieve, the water is separated from the solid particles continuously to a separate stream. Pellet water is recirculated back to the pelletizer in a closed system. Moist particles are withdrawn continuously via a separate sloped sieve or curved sieve which retains pellets on top while allowing pellet water to flow down and routes the retained pellets away from pellet water stream.

The pellets are recovered, stored and shipped to customers.

- 15 The water is recovered, cooled and recycled to the pelletizer.

Pellets

The pellets obtained with the above described pelletization process have advantageous shape and size.

This is expressed i.a. by the so-called shape factor (SPF).

- 20 The shape factor (SPF) describes the shape of the pellets, independent of their size and is, in the context of this invention, the relation between pellet perimeter and area according to formula

$$\text{SPF} = U^2 / (4 \pi A)$$

U = perimeter

- 25 $\pi = \text{pi} (3,14159.....)$

A = area

All shapes, which deviate from the ideal circle form have a shape factor of > 1 .

The pellets obtained with the process of the present invention have a higher amount of pellets having a shape factor (SPF) of below 1.2 compared to pellets obtained without the specific pelletizing agent.

Thus, at least 27%, preferably at least 30% of the pellets obtained with the process of the present invention have a shape factor (SPF) below 1.2.

Preferably, up to 50%, more preferably up to 70%, even more preferably up to 90%, most preferably and ideally 100% of the pellets obtained with the process of the present invention have a shape factor (SPF) below 1.2.

According to the present invention, pellets are defined as having a shape factor of up to 1.4. For those pellets (i.e. having a shape factor of up to 1.4) the size distribution with classes between 1 to 3 mm and between 3 and 5 mm is calculated and their respective sum being the class of 1 to 5 mm is then calculated.

Pellets having a shape factor of up to 1.4 obtained with the process of the present invention have a higher amount of pellets falling into the class of 1 to 5 mm compared to pellets obtained without the specific pelletizing agent.

Thus, at least 85%, preferably at least 88%, more preferably at least 90% of the and ideally 100% of the pellets obtained with the process of the present invention have a particle size distribution between 1 and 5 mm.

Pellets obtained with the process of the present invention additionally have a lower amount of so-called "multiples" compared to pellets obtained without the specific pelletizing agent.

"Multiples" are, according to the present invention, defined as particles being visually identified as stable agglomerates of two or more pellets adhering to each other.

Thus, 0 to below 2.3%, preferably 0 to below 2.0% of the pellets obtained with the process of the present invention are in the form of so-called multiples.

Ideally, 0% of the pellets obtained with the process of the present invention are in the form of so-called multiples.

In one embodiment of the present invention, the pellets obtained with the process of the present invention additionally have a lower amount of so-called "tailed" particles compared to pellets obtained without the specific pelletizing agent.

Tailed particles are defined as otherwise pellet-like particles with a fibrous extension resembling an animal's tail, which is longer than 1000 μm .

Thus, below 4.0%, preferably below 3.5% and more preferably below 3% of the pellets obtained with the process of the present invention are in the form of so-called tailed particles.

Ideally, 0% of the pellets obtained with the process of the present invention are in the form of so-called tailed particles.

- 5 Above described pellet properties are determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

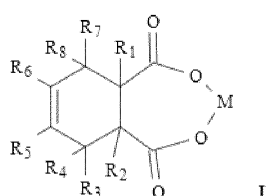
The present invention therefore provides a process for pelletizing soft copolymers of propylene where formation of agglomerated and fused pellets is reduced. Further, the pellets formed in the process can be handled, stored and transported without difficulty.

- 10 The process can be operated in conventional apparatus without additional investment.

In a further embodiment the present invention is related to pellets of polyolefins, comprising a composition of

a polyolefin, preferably a polyolefin copolymer being characterized by

- a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa and
 15 a content of chain units derived from propylene, determined with $^{13}\text{C}\{^1\text{H}\}$ NMR as described in the experimental part, of more than 50 wt.-%, based on the total weight of the soft polyolefin;
 10 to 1000 ppm, based on the total weight of the polyolefin, of a pelletization agent of formula (I)



- 20 wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 are independently selected from H, $\text{C}_1\text{-C}_9$ alkyl, hydroxyl, phenyl, $\text{C}_1\text{-C}_{18}$ -alkylphenyl and halogen, M is metal cation selected from Mg, Ca, Zn, Sr, Ba, La and Eu and

- 500 to 10000 ppm in total, based on the total weight of the polyolefin of one or more additives selected from the group consisting of antioxidants and process stabilisers, UV-stabilisers, heat
 25 stabilisers, slip agents, antiblocking agents, acid scavengers, metal deactivators, antimicrobial agents antistatic agents and pigments,

the pellets being characterized by

a) at least 27%, preferably at least 30% of the pellets having a shape factor (SPF) below 1.2, wherein the shape factor is the relation between pellet perimeter and area according to formula.

5 $SPF = U^2 / (4 \pi A)$

with U = perimeter, π = pi (3,14159.....) and A = projection area,

b) at least 85%, preferably at least 88%, more preferably at least 90% of the pellets having a particle size distribution between 1 and 5 mm,

c) below 2.3%, preferably below 2.0% of the pellets are in the form of multiples and

10 d) below 4.0%, preferably below 3.5% and more preferably below 3% of the pellets are in the form of tailed particles.

Experimental Part

1. Measuring methods

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

5 a) Melt Flow Rate (MFR₂)

The melt flow rate is the quantity of polymer in grams which the test apparatus standardized to ISO 1133 or ASTM D1238 extrudes within 10 minutes at a certain temperature under a certain load.

10 The melt flow rate MFR₂ of propylene based polymers was measured at 230°C with a load of 2.16 kg (MFR_{230/2.16}) according to ISO 1133.

b) Density

The density was measured according to ISO 1183D. The samples preparation is carried out by compression moulding according to ISO 1872-2:2007.

c) Comonomer content

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

Comonomer content quantification of poly(propylene-co-ethylene) copolymers

20 Quantitative ¹³C{¹H} NMR spectra were recorded in the solution-state using a Bruker Advance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for ¹H and ¹³C respectively. All spectra were recorded using a ¹³C optimised 10 mm extended temperature probe head at 125°C using nitrogen gas for all pneumatics. Approximately 200 mg of material was dissolved in 3 ml of 1,2-tetrachloroethane-d₂ (TCE-d₂) along with chromium-(III)-acetylacetonate (Cr(acac)₃) resulting in a 65 mM solution of relaxation agent in solvent {8}. To ensure a homogenous solution, after initial sample preparation in a heat block, the NMR
25 tube was further heated in a rotatory oven for at least 1 hour. Upon insertion into the magnet the tube was spun at 10 Hz. This setup was chosen primarily for the high resolution and quantitatively needed for accurate ethylene content quantification. Standard single-pulse excitation was employed without NOE, using an optimised tip angle, 1 s recycle delay and a bi-level WALTZ16 decoupling scheme {3, 4}. A total of 6144 (6k) transients were acquired per
30 spectra.

Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were processed, integrated and relevant quantitative properties determined from the integrals using proprietary computer programs. All chemical shifts were indirectly referenced to the central methylene group of the ethylene block (EEE) at 30.00 ppm using the chemical shift of the solvent. This approach allowed comparable
 5 referencing even when this structural unit was not present. Characteristic signals corresponding to the incorporation of ethylene were observed {7}.

The comonomer fraction was quantified using the method of Wang et. al. {6} through integration of multiple signals across the whole spectral region in the $^{13}\text{C}\{^1\text{H}\}$ spectra. This method was chosen for its robust nature and ability to account for the presence of regio-
 10 defects when needed. Integral regions were slightly adjusted to increase applicability across the whole range of encountered comonomer contents.

For systems where only isolated ethylene in PPEPP sequences was observed the method of Wang et al. was modified to reduce the influence of non-zero integrals of sites that are known to not be present. This approach reduced the overestimation of ethylene content for such
 15 systems and was achieved by reduction of the number of sites used to determine the absolute ethylene content to:

$$E = 0.5 (S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + 0.5(S_{\alpha\beta} + S_{\alpha\gamma}))$$

Through the use of this set of sites the corresponding integral equation becomes:

$$E = 0.5 (I_H + I_G + 0.5(I_C + I_D))$$

20 using the same notation used in the article of Wang et al. {6}. Equations used for absolute propylene content were not modified.

The mole percent comonomer incorporation was calculated from the mole fraction:

$$E [\text{mol}\%] = 100 * f_E$$

The weight percent comonomer incorporation was calculated from the mole fraction:

$$25 \quad E [\text{wt}\%] = 100 * (f_E * 28.06) / ((f_E * 28.06) + ((1-f_E) * 42.08))$$

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10

d) Differential scanning calorimetry (DSC) analysis, melting temperature (T_m) and crystallization temperature (T_c):

measured with a TA Instrument Q2000 differential scanning calorimetry (DSC) on 5 to 7 mg samples. DSC was run according to ISO 11357 / part 3 /method C2 in a heat / cool /heat cycle
15 with a scan rate of 10 °C/min in the temperature range of -30 °C to +225 °C.

Crystallization temperature and heat of crystallization (H_c) were determined from the cooling step, while melting temperature and heat of fusion (H_f) were determined from the second heating step.

e) Flexural Modulus

20 The flexural modulus was determined according to ISO 178 at a test speed of 2 mm/min and a force of 100 N, whereby the length of the span between the supports was 64 mm, on test specimens having a dimension of 80x10x4 mm³ (length x width x thickness) prepared by injection moulding according to EN ISO 1873-2.

f) Xylene cold solubles (XCS) content

25 was measured at 25 °C according to ISO 16152, first edition; 2005-07-01.

g) CRYSTEX QC analysis

Crystalline and soluble fractions method

The crystalline (CF) and soluble fractions (SF) of the polypropylene (PP) compositions as well as the comonomer content and intrinsic viscosities of the respective fractions were analyzed
30 by use of the CRYSTEX instrument, Polymer Char (Valencia, Spain). Details of the technique and the method can be found in literature (Ljiljana Jeremic, Andreas Albrecht, Martina Sandholzer & Markus Gahleitner (2020) Rapid characterization of high-impact ethylene-

propylene copolymer composition by crystallization extraction separation: comparability to standard separation methods, International Journal of Polymer Analysis and Characterization, 25:8, 581-596)

5 The crystalline and amorphous fractions were separated through temperature cycles of dissolution at 160 °C, crystallization at 40 °C and re-dissolution in 1,2,4-trichlorobenzene at 160 °C. Quantification of SF and CF and determination of ethylene content (C2) were achieved by means of an integrated infrared detector (IR4) and for the determination of the intrinsic viscosity (IV) an online 2-capillary viscometer was used.

10 The IR4 detector was a multiple wavelength detector measuring IR absorbance at two different bands (CH₃ stretching vibration (centred at app. 2960 cm⁻¹) and the CH stretching vibration (2700-3000 cm⁻¹) that were serving for the determination of the concentration and the Ethylene content in Ethylene-Propylene copolymers. The IR4 detector was calibrated with series of 8 EP copolymers with known Ethylene content in the range of 2 wt.-% to 69 wt.-% (determined by ¹³C-NMR) and each at various concentrations, in the range of 2 and 13mg/ml. To encounter
15 for both features, concentration and ethylene content at the same time for various polymer concentrations expected during Crystex analyses the following calibration equations were applied:

$$\text{Conc} = a + b \cdot \text{Abs}(\text{CH}) + c \cdot (\text{Abs}(\text{CH}))^2 + d \cdot \text{Abs}(\text{CH}_3) + e \cdot (\text{Abs}(\text{CH}_3))^2 + f \cdot \text{Abs}(\text{CH}) \cdot \text{Abs}(\text{CH}_3)$$

20 (Equation 1)

$$\text{CH}_3/1000\text{C} = a + b \cdot \text{Abs}(\text{CH}) + c \cdot \text{Abs}(\text{CH}_3) + d \cdot (\text{Abs}(\text{CH}_3)/\text{Abs}(\text{CH})) + e \cdot (\text{Abs}(\text{CH}_3)/\text{Abs}(\text{CH}))^2$$

(Equation 2)

25 The constants a to e for equation 1 and a to f for equation 2 were determined by using least square regression analysis.

The CH₃/1000C is converted to the ethylene content in wt.-% using following relationship:

$$\text{Wt.-% (Ethylene in EP Copolymers)} = 100 - \text{CH}_3/1000\text{TC} \cdot 0.3$$

(Equation 3)

30

Amounts of Soluble Fraction (SF) and Crystalline Fraction (CF) are correlated through the XS calibration to the "Xylene Cold Soluble" (XCS) quantity and respectively Xylene Cold Insoluble (XCI) fractions, determined according to standard gravimetric method as per ISO16152. XS

calibration is achieved by testing various EP copolymers with XS content in the range 2-31 wt.-%. The determined XS calibration is linear:

$$\text{Wt.-% XS} = 1,01 * \text{Wt.-% SF} \quad (\text{Equation 4})$$

Intrinsic viscosity (IV) of the parent EP copolymer and its soluble and crystalline fractions were determined with a use of an online 2-capillary viscometer and were correlated to corresponding IV's determined by standard method in decalin according to ISO 1628-3. Calibration was achieved with various EP PP copolymers with IV = 2-4 dL/g. The determined calibration curve is linear:

$$\text{IV (dL/g)} = a * \text{Vsp/c} \quad (\text{equation 5})$$

10

The samples to be analyzed were weighed out in concentrations of 10mg/ml to 20mg/ml. To avoid injecting possible gels and/or polymers, which do not dissolve in TCB at 160 °C, like PET and PA, the weighed out sample was packed into a stainless steel mesh MW 0,077/D 0,05mmm.

15 After automated filling of the vial with 1,2,4-TCB containing 250 mg/l 2,6-tert-butyl-4-methylphenol (BHT) as antioxidant, the sample was dissolved at 160 °C until complete dissolution is achieved, usually for 60 min, with constant stirring of 400rpm. To avoid sample degradation, the polymer solution is blanketed with an N₂ atmosphere during dissolution.

20 A defined volume of the sample solution was injected into the column filled with inert support where the crystallization of the sample and separation of the soluble fraction from the crystalline part was taking place. This process was repeated two times. During the first injection the whole sample was measured at high temperature, determining the IV[dL/g] and the C2[wt.-%] of the PP composition. During the second injection the soluble fraction (at low temperature) and the crystalline fraction (at high temperature) with the crystallization cycle
25 were measured (wt.-% SF, wt.-% C2, IV).

h) Intrinsic viscosity

The intrinsic viscosity (iV) was measured according to DIN ISO 1628/1, October 1999, in Decalin at 135 °C.

30 i) Instrumental pellet contamination, shape and size measurements

Determination of pellet contamination, shape and size was done using a PA66 device consisting a Pellet Contamination Analysing System (PS25C) and a Pellet Shape and Size Distribution (PSSD) system from OCS GmbH (Witten, Germany).

5 PS25C: The pellets were transported under a high speed CCD (Charge-coupled device) camera and images were taken. Based on their colour spectrum they were divided into several classes.

10 PSSD: Pellets were transported by a vibration unit. A high speed line-sensor recorded their 2-dimensional picture in free falling mode. The system measured the size of the pellets in different size and shape classes, categorizing the analyzed particles into pellets, dust and other shape-deviating particles like tailed particles, multiples and the like.

For the present invention, only the parameters of the particle size and shape distribution (PSSD) are relevant. For this, first the pellet size was determined as the equivalent circle diameter of a particle's projection, followed by a size classification. Subsequently, other parameters of the particle shape were calculated:

15 - The shape factor (SPF) describes the shape of the pellets, independent of their size and is, in the context of this invention, the relation between pellet perimeter and area according to formula.

$$\text{SPF} = U^2 / (4 \pi A),$$

20 with U being the perimeter, π being the parameter pi (3,14159....) and A the projection area of the particle. All shapes, which deviate from the ideal circle form have a shape factor of > 1.

- "Pellets" are defined as having a shape factor of up to 1.4. All other particles have to be categorized as "dust", "multiples", "longs", "tailed", "angel hair", "miscuts" or "other".

25 - The fraction of "dust" is defined as particles having a projection size (largest dimension) of less than 1 mm.

- The fraction of "multiples" is defined as particles being visually identified as stable agglomerates of two or more pellets adhering to each other. Such particles are commonly formed by agglomeration of polymer melt after cutting in the water bath, and their presence is highly undesirable.

30 - The fraction of "longs" is defined as particles of high aspect ratio, their length being at least twice their diameter, but otherwise regular shape.

- The fraction of "tailed" is defined as otherwise pellet-like particles with a fibrous extension resembling an animal's tail longer than 1000 µm, caused by bad cut.
- The fraction of "angel hair" is defined as fibrous particles of straight or curved appearance.
- The fraction of "miscuts" is defined as fragments between 1 and 3 mm projection size (largest dimension) and a shape factor of > 1.45.
- All other particles are subsumed as "other".
- The average pellet size is calculated as number of pellets per gram of polymer (pcs/g).
- The size distribution with classes of 1 – 3 mm and 3 – 5 mm is calculated for "pellets" only, their respective sum being the class of 1 – 5 mm.
- The general content of all particles is additionally calculated for the size range of 3 – 5 mm.

2. Experimental part

Preparation of soft polyolefin (RAHECO)

• Catalyst

The catalyst used in the polymerization process for the heterophasic propylene copolymer RAHECO has been produced as follows: First, 0.1 mol of $\text{MgCl}_2 \times 3 \text{ EtOH}$ was suspended under inert conditions in 250 ml of decane in a reactor at atmospheric pressure. The solution was cooled to the temperature of -15°C and 300 ml of cold TiCl_4 was added while maintaining the temperature at said level. Then, the temperature of the slurry was increased slowly to 20°C . At this temperature, 0.02 mol of dioctylphthalate (DOP) was added to the slurry. After the addition of the phthalate, the temperature was raised to 135°C during 90 minutes and the slurry was allowed to stand for 60 minutes. Then, another 300 ml of TiCl_4 was added and the temperature was kept at 135°C for 120 minutes. After this, the catalyst was filtered from the liquid and washed six times with 300 ml heptane at 80°C . Then, the solid catalyst component was filtered and dried. Catalyst and its preparation concept is described in general e.g. in patent publications EP491566, EP591224 and EP586390. As co-catalyst triethyl-aluminium (TEAL) and as donor dicyclo pentyl dimethoxy silane (D-donor) was used.

• Polymerization of Heterophasic propylene copolymer RAHECO

Heterophasic propylene copolymer RAHECO has been produced in a Borstar™ plant in the presence of the above described polymerization catalyst using one prepolymerization reactor, one liquid-phase loop reactor and two gas phase reactors connected in series under conditions as shown in Table 1. The first reaction zone was a loop reactor and the second and third reaction zones were gas phase reactors.

Table 1: Polymerization conditions of heterophasic propylene copolymer RAHECO:

		RAHECO
Prepolymerization		
TEAL	[kg/h]	4.1
Donor	[kg/h]	0.66
Temperature	[°C]	20
res.time	[h]	0.33
Loop		
Temperature	[°C]	70
Split	[%]	15
H2/C3 ratio	[mol/kmol]	5.5
C2-feed	[kg/h]	253
MFR ₂	[g/10min]	6.0
XCS	[wt.-%]	3.0
C2	[wt.-%]	2.0
GPR 1		
Temperature	[°C]	75
Pressure	[barg]	21.3
Split	[%]	60
H2/C3 ratio	[mol/kmol]	21.8
C2/C3 ratio	[mol/kmol]	63.0
MFR ₂	[g/10min]	1.7
XCS	[wt.-%]	22.0
C2 content	[wt.-%]	6.5
GPR 2		

Temperature	[°C]	80
Pressure	[barg]	15
Split	[%]	25
C2/C3 ratio	[mol/kmol]	400
H2/C2 ratio	[mol/kmol]	180
MFR ₂	[g/10min]	2.0
C2 content (total)	[wt.-%]	12.7
SF	[wt.-%]	35.7
C2(SF)	[wt.-%]	27.2
C2(CF)	[wt.-%]	5.18
IV(SF)	dL/g	2.61

RAHECO has a melt flow rate MFR₂ (230 °C, 2.16 kg) of 2.0 g/10 min, a flexural modulus of 330 MPa and a melting temperature T_m of 151 °C.

5 The polymer was withdrawn from the reactor and introduced into a ZSK 59 extruder, where it was mixed with effective amounts (1400 ppm in total) of Irgafos 168 (812 ppm), Irganox 1010 (406 ppm) and MgO (182 ppm). (CE1)

For inventive example 1, in addition 50 ppm of Sipax NAB-82 commercially available from GCH, (4-Cyclohexene-1,2-dicarboxylic acid, calcium salt (1:1) (CAS 57545-78-5)) have been added as pelletizing agent.

10 For CE2 1000 ppm of Erol RTBN was added instead of Sipax NAB-82.

Erol RTBN is a defoamer, commercially available from PMC OUVRIE and is used in the state of the art to prevent agglomeration.

15 The used ZSK 59 extruder was equipped with a down-scaled screw from production extruder CMP 362. As the ZSK 59 has a longer L/D than the CMP 362, the temperatures in the first zones were kept at low temperature and only used for powder conveying. Process parameters can be seen in Table 2, the temperature profile of the extruder is shown in Table 3.

Table 2: Process parameters:

		Units
Throughput	185	kg/h
Melt temperature	225	°C
PCW temperature	30-32	°C
Screw speed	400	RPM
SEI	0,4	kWh/kg
Die plate pressure	63	barG
PCW flowrate	25.4	m³/h
Die plate	12 x 2,8	Amount x mm
Melt pump used	No	-

SEI: specific energy input

PCW: pellet cooling water

Table 3: Temperature profile [°C]

Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10	Z11	Die plate
-	80	80	190	220	250	200	240	280	240	250	220

5

- The used under water pelletizing system was a GALA TWS20 system (TWS: tempered water system), provided by Gala Industries. 90-95% of the water was separated already in the pre-dewatering step of the Gala System. Then the pellets went in the lower third of the centrifuge, where the pellets hit the sieve and rotor separating the surface water from the pellets. (The rpm of the centrifuge is fixed by the supplier) A suction system was generating an airflow in counter direction of the pellets. The counter flow was taking up residual moisture of the pellet surface and is avoiding transportation of water and humid air with the pellets. The combination of the centrifuge and the counter air flow were the main drying steps in this system. The air flow had room temperature.
- 10
- 15 After the drying step there was a sieve to avoid dust or too big pellets and agglomerations in the product. The pellets were mainly dry already when leaving the centrifuge.

Table 4: Pellet properties of IE and CEs

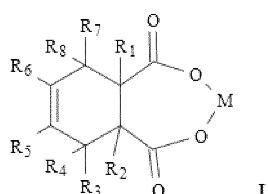
		CE1	CE2	IE1
Measurement	Unit	RAHECO	RAHECO + Erol RTBN 1000 ppm	RAHECO +0.005wt% SIPAX NAB- 82
Pellet size	pcs/g	50	53	55
SPF < 1,2	%	26.1	21.9	31.1
Pellets 1-3 mm	%	4.5	2.8	3.6
Pellets 3-5 mm	%	79.9	80.5	88.4
Pellets 1-5 mm	%calc	84.4	83.3	92
Tailed	%	5.2	6.2	2.5
Longs	%	0.5	0.3	0.2
Multiples	%	5.2	2.5	1.9
Angel Hair	%	0.2	0.2	0.2
Miscuts	%	0.2	0.3	0.2
Unknown	%	4.4	7.3	3
Dust	%	4.1	3.1	0.8

As can be seen from the Table above, pellets prepared by the inventive method have a higher amount of pellets having a shape factor (SPF) of below 1.2, a higher amount of pellets having particle size distribution between 1 and 5 mm, less tailed particles and less multiples compared to pellets obtained without the specific pelletizing agent.

5

Claims:

1. A process for producing pellets of polyolefins, the process comprising the steps of
- i-a) introducing a soft polyolefin, the soft polyolefin being characterized by
- a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa and
- 5 a content of chain units derived from propylene, determined with $^{13}\text{C}\{^1\text{H}\}$ NMR as described in the experimental part, of more than 50 wt.-%, based on the total weight of the soft polyolefin;
- i-b) 10 to 1000 ppm, based on the total weight of the soft polyolefin, of a pelletization agent of formula (I)



- 10 wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 are independently selected from H, C_1 - C_9 alkyl, hydroxyl, phenyl, C_1 - C_{18} - alkylphenyl and halogen, M is metal cation selected from Mg, Ca, Zn, Sr, Ba, La and Eu and
- i-c) 500 to 10000 ppm in total, based on the total weight of the soft polyolefin of one or more additives selected from the group consisting of antioxidants and process stabilisers, UV-
- 15 stabilisers, heat stabilisers, slip agents, antiblocking agents, acid scavengers, metal deactivators, antimicrobial agents antistatic agents and pigments and mixtures thereof
- into a type of continuous mixer,
- ii) melting the i-a) polyolefin containing the pelletization agent i-b) and additives i-c) forming a molten polyolefin composition,
- 20 iii) extruding the molten polyolefin composition through a die plate having a multitude of holes into a pellet water bath in a pelletizer thereby producing strands of the polyolefin composition and solidifying the strands,
- iv) cutting the strands of the polyolefin composition in the pelletizer into pellets, and
- v) drying the pellets.

2. Process according to claim 1, wherein the soft polyolefin is a propylene copolymer with ethylene and/or 1-butene comonomer(s) with a soluble fraction content, determined according to the CRYSTEX QC method as described in the experimental part, in the range of 20 to 80 wt.-%, based on the propylene copolymer, more preferably a random-heterophasic propylene-ethylene copolymer (RAHECO) comprising
- 5
- a) a crystalline matrix (M) being a propylene-ethylene random copolymer; and
 - b) an amorphous propylene-ethylene elastomer (E).
3. Process according to claim 2, wherein the random-heterophasic propylene-ethylene copolymer (RAHECO) has
- 10
- an ethylene content (C2(total)), determined by FT-IR spectroscopy calibrated by quantitative ¹³C-NMR spectroscopy in the CRYSTEX QC method, in the range from 3.0 to 25.0 wt.-%, more preferably in the range from 5.0 to 20.0 wt.-%, most preferably in the range from 8.0 to 15.0 wt.-%;
- a soluble fraction (SF) content, based on the total amount of the RAHECO, determined according to CRYSTEX QC analysis, in the range from 20 to 80 wt.-%, more preferably in the range from 25 to 60 wt.-%, most preferably in the range from 30 to 50 wt.-%;
- 15
- an ethylene content of the soluble fraction (C2(SF)), according to CRYSTEX QC analysis, determined by FT-IR spectroscopy calibrated by quantitative ¹³C-NMR spectroscopy in the CRYSTEX QC method, in the range from 20 to 80 wt.-%, more preferably in the range from 23 to 60 wt.-%, most preferably in the range from 25 to 50 wt.-% and
- 20
- an intrinsic viscosity, determined according to DIN ISO 1628/1, of the soluble fraction (iV(SF)), according to CRYSTEX QC analysis, in the range from 1.20 to 6.0 dL/g, more preferably in the range from 1.50 to 5.0 dL/g, most preferably in the range from 2.0 to 4.0 dL/g.
4. Process according to claim 2 or 3, wherein the random-heterophasic propylene-ethylene copolymer (RAHECO) has
- 25
- a melt flow rate (MFR₂), determined according to ISO 1133 at 230 °C and 2.16 kg, in the range from 0.1 to 100 g/10 min, more preferably in the range from 0.3 to 50.0 g/10 min, even more preferably in the range from 0.5 to 20.0 g/10 min and most preferably in the range of 0.8 to 10.0 g/ 10 min and

a melting temperature (T_m), determined by differential scanning calorimetry (DSC), in the range from 130 °C to 160 °C, more preferably of from 140 °C to 157 °C and most preferably of from 145 °C to 155 °C.

5. The process according to any one of the preceding claims wherein the pelletizing agent of formula (I) with R_1 to R_8 being independently selected from the group consisting of hydrogen and C_1 - C_4 -alkyl, more preferably from hydrogen, methyl and ethyl, most preferably each of R_1 to R_8 are hydrogen and

M being a metal cation selected from Mg, Ca, Zn, La, more preferably M is Ca or Zn, most preferably Ca.

- 10 is used.

6. The process according to any one of the preceding claims wherein the pelletizing agent of formula (I) is added in an amount of 15 to 500 ppm, more preferably in an amount of 20 to 100 ppm and most preferably in an amount of 25 to 80 ppm, based on the total weight of the polyolefin.

- 15 7. The process according to any one of the preceding claims wherein

in step i) the polyolefin, which has been removed from the polymerization reactor in powder form, the pelletizing agent and the further additives are introduced into an extruder, whereby the extrusion is conducted in a twin screw extruder.

8. The process according to any one of the preceding claims wherein

- 20 in step ii) for melting the polyolefin i-a) containing the pelletization agent i-b) and additives i-c) in the extruder forming a molten polyolefin composition the temperature in the extruder is adjusted to a range of from 150 to 300 °C, preferably from 170 to 290 °C, whereby the melt temperature in the extruder at or close to the die plate is adjusted to a range of from 190 to 250 °C, preferably from 200 to 240 °C.

- 25 9. The process according to any one of the preceding claims wherein

in step iii) and iv) the pellets are formed by extruding the polymer melt through the holes in the die plate to strands, whereby the strands pass through the die plate into a water bath in an underwater pelletizer, the temperature of the pellet water in the pelletizer being in the range from 10 to 70 °C, and

whereby at or immediately after the die plate a set of rotating knives, which cut the strands to pellets is placed and water is continuously added to the bath and slurry comprising the water and the pellets is continuously withdrawn from the pelletizer.

10. The process according to any one of the preceding claims wherein

- 5 the die plate has a multiple of openings through which the molten polymer flows into the pelletizer, whereby the openings have typically a diameter of from 2.0 to 3.0 mm.

11. The process according to any one of the preceding claims wherein

at least 27%, preferably at least 30% of the pellets obtained with the process as described in claims 1 to 10 have a shape factor (SPF) below 1.2, wherein the shape factor is the relation

- 10 between pellet perimeter and area according to formula

$$\text{SPF} = U^2 / (4 \pi A)$$

with U = perimeter, π = pi (3,14159.....) and A = projection area; the shape factor being determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

- 15 12. The process according to any one of the preceding claims wherein at least 85%, preferably at least 88%, more preferably at least 90% of the pellets obtained with the process as described in claims 1 to 11 have a particle size distribution between 1 and 5 mm, the particle size distribution being determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

- 20 13. The process according to any one of the preceding claims wherein below 2.3%, preferably below 2.0% of the pellets obtained with the process as described in claims 1 to 12 are in the form of multiples; the percentage of multiples being determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

- 25 14. The process according to any one of the preceding claims wherein below 4.0%, preferably below 3.5% and more preferably below 3% of the pellets obtained with the process as described in claims 1 to 13 are in the form of tailed particles, the percentage of tailed particles being determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

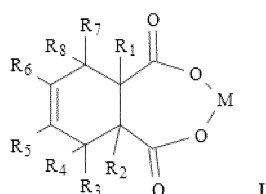
15. Pellets of soft polyolefins, comprising a composition of

- 30 a soft polyolefin, preferably a polyolefin copolymer being characterized by

a flexural modulus determined according to ISO 178 in the range of 10 to below 600 MPa and a content of chain units derived from propylene, determined with $^{13}\text{C}\{^1\text{H}\}$ NMR as described in the experimental part, of more than 50 wt.-%, based on the total weight of the soft polyolefin;

10 to 1000 ppm, based on the total weight of the polyolefin, of a pelletization agent of formula

5 (I)



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 are independently selected from H, $\text{C}_1\text{-C}_9$ alkyl, hydroxyl, phenyl, $\text{C}_1\text{-C}_{18}$ -alkylphenyl and halogen, M is metal cation selected from Mg, Ca, Zn, Sr, Ba, La and Eu and

10 500 to 10000 ppm in total, based on the total weight of the polyolefin of one or more additives selected from the group consisting of antioxidants and process stabilisers, UV-stabilisers, heat stabilisers, slip agents, antiblocking agents, acid scavengers, metal deactivators, antimicrobial agents antistatic agents and pigments,

the pellets being characterized by

15 a) at least 27%, preferably at least 30% of the pellets having a shape factor (SPF) below 1.2, wherein the shape factor is the relation between pellet perimeter and area according to formula

$$\text{SPF} = U^2 / (4 \pi A)$$

with U = perimeter, π = pi (3,14159.....) and A = projection area,

b) at least 85%, preferably at least 88%, more preferably at least 90% of the pellets having a
20 particle size distribution between 1 and 5 mm,

c) below 2.3%, preferably below 2.0% of the pellets are in the form of multiples and

d) below 4.0%, preferably below 3.5% and more preferably below 3% of the pellets are in the form of tailed particles, whereby the properties a, b, c and d are determined by Instrumental pellet contamination, shape and size measurements as described in the experimental part.

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