Title: PROCESS FOR MANUFACTURING ETHYLENE POLYMERS AND COPOLYMERS

Abstract: A process for producing ethylene polymer in a tubular reactor includes compressing ethylene monomer to a pressure between 2000 bar and 2300 bar; heating the ethylene monomer to a temperature between 135°C and 200°C; introducing initiator into the tubular reactor in at least five separate locations, thereby defining at least five reaction zones; and separating the ethylene polymer from the reaction mixture; wherein the ethylene polymer has a polydispersity, Mw/Mn, no less than 7.0.
PROCESS FOR MANUFACTURING
ETHYLENE POLYMERS AND COPOLYMERS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of Serial No. 61/986,538, filed April 30, 2014, the disclosure of which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

This application relates to the polymerization of polyolefin polymers, primarily using high pressure polymerization processes.

BACKGROUND OF THE INVENTION

High pressure reactor polymerization plants convert relatively low cost olefin monomer (generally ethylene, optionally in combination with one or more comonomers such as vinyl acetate) into valuable polyolefin product. Such processes using oxygen or organic free-radical initiators, in particular peroxide initiators, are known in the art and have been used in industry for a long time. The polymerization takes place at relatively high temperatures and pressures and is highly exothermic. The resulting polymer is a low density polyethylene (LDPE), optionally containing comonomers. See, for example, Ullmann's Encyclopedia of Technical Chemistry, 4th edition, Vol. 19, 1980, pp. 169-178.

High pressure polymerization processes are carried out in autoclave or tubular reactors. In principle, the autoclave and the tubular polymerization processes are similar, except for the design of the reactor itself. The plants generally use two main compressors to compress the monomer feed each with multiple stages, arranged in series: a primary compressor provides an initial compression of the monomer feed, and a secondary (high pressure) compressor increases the pressure generated by the primary compressor to the level at which polymerization takes place in the reactor, which is typically in excess of 2300 bar and sometimes as high as 3100 bar for a tubular reactor and about 120 bar to about 200 bar for an autoclave reactor.

One important application for LDPE is extrusion coating, which is a process in which molten LDPE resin is applied to a substrate material such as paper, board, plastic film, or metal foil. An uninterrupted melt web is necessary for successful extrusion coating, thus requiring LDPE of even and exceptional quality. Neck-in and draw down are two specific properties that indicate the performance of a polymer with regard to extrusion coating. Neck-in is the reduction of film width. High neck-in is not desirable as it may cause edge areas of the substrate to not be coated, thus requiring trimming after the coating process. Draw down is the ability of the melt web to be drawn to thin films at high speeds without breaking. High
draw down is preferred so the extrusion coating can successfully be run at high production speeds.

[0006] Autoclave reactors have generally been preferred over tubular reactors for creating extrusion coating grade LDPE because autoclave reactor-produced LDPE exhibits a balance of neck-in vs. draw down more suitable to the application than tubular reactor-produced LDPE of similar density. This is because autoclave reactor-produced LDPE tends to have a broader molecular weight distribution (MWD), or polydispersity, and more long chain branching (LCB) than tubular reactor-produced LDPE.

[0007] However, production of LDPE by tubular reactor is generally more economical, efficient, and easier to implement on large scales. WO 2007/018871, for example, describes a tubular reactor over 300 kilotonnes per annum.

[0008] WO 2013/083285 describes a process for producing low density polyethylene in a tubular reactor by using three times the conventional amount of used active oxygen, i.e., radical initiators in order to induce long chain branching and increased weight average molecular weight.

[0009] WO 2013/078018 describes an ethylene based polymer with a melt index over (12) 2.0 dg/min and a weight average molecular weight (Mw) ≥ G + H(I2) where G=1.70 x 10^5 g/mole and H = -8.00 x 10^-3 g/mole)/(dg/min) using chain transfer agents, such as acetone, to control number average molecular weight and the melt index. In numerous embodiments, the ethylene based polymer is produced in a tubular reactor with three reaction zones using a special high temperature peroxide initiator 3,6,9-triethyl 3,6,9-trimethyl 1,4,9-peroxononane resulting in high peak temperatures.

[0010] US 7820776 describes a process for the preparation of ethylene copolymers with certain web stability, neck-in, and draw down properties. The comonomer is di- or higher functional (meth)acrylate.

[0011] There is therefore a need for a process for producing low density polyethylene suitable for extrusion coating applications utilizing a tubular reactor that overcomes traditional neck-in and draw down deficiencies without resorting to the use of special or exotic comonomers, chain transfer agents, and/or initiators, or large amounts of initiator which require incurring high costs for the additional reactants and physical plant components necessary to incorporate them.

**SUMMARY OF THE INVENTION**

[0012] More specifically, the present inventive process comprises (1) compressing ethylene monomer in one or more compressors to a pressure between 2000 bar and 2300 bar;
(2) heating the ethylene monomer to a temperature between 135°C and 200°C;
(3) introducing the compressed, heated ethylene monomer into a front end of a tubular reactor; (4) introducing initiator into the tubular reactor in at least five separate locations, thereby defining at least five reaction zones where the ethylene monomer polymerizes forming a reaction mixture comprising unreacted ethylene monomer and ethylene polymer; and (5) separating the ethylene polymer from the reaction mixture; wherein the ethylene polymer has a polydispersity, Mw/Mn, no less than 7.0.

The present invention provides a reliable method of manufacture of ethylene polymer with a broad MWD necessary for extrusion coating applications while avoiding the high costs of utilizing exotic comonomers, chain transfer agents, and large amounts of initiator and the inefficiencies of using an autoclave reactor through the addition of reaction zones and specific control of reaction pressure and temperature at each of the reaction zones.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows schematically an ethylene polymerization plant or apparatus according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

A process for producing ethylene polymer comprising (1) compressing ethylene monomer in one or more compressors to a pressure between 2000 bar and 2300 bar; (2) heating the ethylene monomer to a temperature between 135°C and 200°C; (3) introducing the compressed, heated ethylene monomer into a front end of a tubular reactor; (4) introducing initiator into the tubular reactor in at least five separate locations, thereby defining at least five reaction zones where the ethylene monomer polymerizes forming a reaction mixture comprising unreacted ethylene monomer and ethylene polymer; and (5) separating the ethylene polymer from the reaction mixture; wherein the ethylene polymer has a polydispersity, Mw/Mn, of no less than 7.0, and is hereinafter discussed in detail, with reference to Fig. 1.

Fig. 1 is a schematic of a polymerization plant 1 including an ethylene feed line 2 which supplies fresh ethylene to a primary compressor 3. The ethylene discharged from primary compressor 3 flows via conduit 4 having a valve 4a to the secondary compressor 5. A modifier stream is supplied by a separate modifier pump 6. Recycled ethylene is supplied from a high pressure recycle system 7.

Secondary compressor 5 is described in more detail below. The secondary compressor 5 discharges compressed ethylene into multiple streams, a main feed stream 8a, and a plurality of sidestreams. The number of sidestreams may vary between 2 and 4, and in
one class of embodiments, the number of sidestreams may be 3, as depicted in Fig. 1, as 8b, 8c, and 8d. Stream 8a accounts for about 33% of the total ethylene flow. Stream 8a is heated by a steam jacket (not shown) which heats the ethylene, prior to entry into the front end of the tubular reactor 9. The remaining ethylene sidestreams 8b, 8c, and 8d each enter at various points along the reactor after being cooled. Sidestreams 8b, 8c, and 8d may contain fresh ethylene, recycled ethylene, or a combination of both.

Tubular reactor 9 has a plurality of initiator inlets. The number of initiator inlets may vary between 4 and 7, but is preferably at least 5, as is depicted in Fig. 1 as 10a to 10e, which are spaced at intervals along reactor 9 and are fed from an initiator mixing and pumping station 11. First initiator injection point 10a is just downstream of the front end of the reactor 9 and defines the start of the first reaction zone. Initiator entering through first initiator inlet 10a combines with the hot ethylene from stream 8a and polymerization begins, raising the temperature of the ethylene as it travels down tubular reactor 9. The temperature of the reaction mixture peaks at between 275°C and 350°C, as initiator is consumed and the rate of polymerization begins to fall, and then begins to decline as a heating/cooling jacket (not shown) fitted on reactor 9 cools the reaction mixture. Entry of first sidestream 8b cools the reaction mixture further. Second initiator injection inlet 10b is just downstream of the entry point of sidestream 8b and defines the start of the second reaction zone. Once again, the temperature of the reaction mixture rises, peaks and falls as it flows along tubular reactor 9 with the entry of the second sidestream 8c providing a further rapid cooling prior to entry of initiator at the third initiator inlet 10c, which defines the start of the third reaction zone. The third and fourth reaction zones are similar to the second reaction zone, the start of each defined by initiator inlets 10c and 10d just downstream of the introduction of sidestreams 8c and 8d respectively. The fifth reaction zone, the start of which is defined by initiator inlet 10e, may not have an ethylene sidestream immediately upstream of it, thus the reaction mixture downstream of the fourth and fifth reaction zones may be cooled through reactor sections surrounded by cooling jackets. The distances between the fourth and fifth initiator inlets 10e and 10d and between fifth initiator inlet 10e and a high-pressure let-down valve 12, which terminates reactor 9 at the downstream end, therefore may be longer than the distances between the preceding initiator inlets in order to allow for a greater length heating/cooling jacket. In an alternative embodiment, the fifth reaction zone is similar to the second reaction zone and has an ethylene sidestream introduced directly upstream of the reaction zones.

In the region upstream of the injection point of first sidestream 8b, the tubular reactor 9 has an initial internal diameter, which increases downstream of sidestream 8b, and
increases further downstream of each subsequent sidestream until a maximum internal diameter of at least 65 mm, and preferably at least 70 mm, is reached in the region downstream of the final sidestream 8d. The internal diameter profile along the length of the reactor allows the velocity throughout the tubular reactor 9 to be maintained at a substantially constant value during normal operation and at an acceptably low pressure drop across the reactor.

[0020] High-pressure, let-down valve 12 controls the pressure in tubular reactor 9. Immediately downstream of the high-pressure, let-down valve 12 is product cooler 13. Upon entry to product cooler 13, the reaction mixture is in a phase separated state. It exits into high pressure separator 14. The overhead gas from high pressure separator 14 flows into high pressure recycle system 7 where the unreacted ethylene is cooled and returned to secondary compressor 5 in embodiments utilizing a recycle stream.

[0021] The polymer product flows from the bottom of high pressure separator 14 into low pressure separator 15, separating almost all of the remaining ethylene from the polymer. The remaining ethylene is transferred either to a flare (not shown) or a purification unit (not shown) or is recycled via primary compressor 3 from the product separator unit to secondary compressor 5. Molten polymer flows from the bottom of low pressure separator 15 to an extruder (not shown) for extrusion, cooling, and pelletizing.

[0022] Operating the tubular reactor at minimum pressure promotes mechanical reliability and energy savings by requiring lighter compressor loads and importantly supports the growth of long chain branches within the reaction mixture, particularly in conjunction with specific temperature ranges at the reaction zones, as described below.

[0023] Long chain branching is a bimolecular and/or intermolecular reaction which occurs through the free radical chain transfer reaction occurring when a peroxy radical or more usually a free radical of one growing polymer chain abstracts a hydrogen from somewhere in another polymer chain. This occurs because (1) there are many more secondary and tertiary hydrogen atoms along the other polymer chain than primary hydrogen atoms at the ends of the growing polymer chain on the chain ends and (2) the ease of hydrogen abstraction, in terms of energy required, decreases in order from tertiary to secondary to primary. The new radical on the other polymer chain will not be at the chain end. This secondary or tertiary radical propagates further chain growth giving rise to a long chain branch. In practice there are many such chain transfers occurring to any one molecule during its residence time in the reactor, thus leading to a highly branched structure.
This chain transfer mechanism leading to long chain branching increases with rising reactor polymer concentration, with higher reactor temperatures, particularly above 200°C, lower reactor pressures, and higher residence time. Lowering the pressure decreases the ethylene density in turn lowering the concentration of ethylene monomer around the radical. This decreases the probability that the radical will propagate further with another ethylene molecule rather than long chain branching.

Because increased long chain branching promotes beneficial resin characteristics for extrusion coating such as lower neck in, it is an overall object of this invention to limit the pressure drop across the reactor through various reactor configuration choices, while still achieving good ethylene conversion rate and long residence time without having to rely on special initiators or initiator overdosing. Some reactor configuration choices must therefore balance the goal of low pressure drop with other potential detrimental effects, thus leading to optimized configuration parameters, which are explained more fully below.

For example, in order to minimize the pressure drop across the reactor, it is necessary to maintain a steady velocity throughout the reactor, which may be accomplished by adjusting, and generally by increasing, the internal diameter of the reactor along its length, particularly as additional volume is introduced (e.g., through sidestreams).

The velocity of the reaction mixture through the reactor is believed to be of critical importance to the effectiveness of the heat transfer out of the reactor. It is theorized that at low velocity laminar flow and build-up of thicker layers of polymer on the inside of the reactor tubes inhibits heat transfer away from the reaction mixture. The actual minimum desirable flow velocity depends on the temperature of the cooling jacket. Where the cooling jacket contains fluid at a temperature below 50°C, and particularly below 30°C, such as water which is maintained at low temperature by cooling means such as a cooling tower, then the flow velocity will preferably be at least 14 m/s in order to inhibit formation of a solid polymer layer on the inside of the tubular reactor which itself further inhibits heat transfer (even then, it may be necessary to allow the temperature of the cooling jacket in a particular reaction zone to rise periodically, in order to disperse any polymer layer which has formed). Accordingly, the flow velocity may be in excess of 14 m/s and is advantageously higher, for example, in the range of from 14m/s to 20 m/s. However, the pressure drop over the length of the reactor is limited by the requirement that the pressure must not fall below the point at which phase separation for the reaction mixture occurs. The pressure drop for a given throughput is reduced by keeping the velocity of the reaction mixture relatively constant by gradually increasing the internal diameter of the tubular reactor along its length until a
maximum internal diameter of at least 65 mm, and preferably at least 70 mm, is reached in the region downstream of the final sidestream.

[0028] Additionally, shortening the overall length of the reactor decreases the overall pressure drop; however, doing so can reduce the number of reaction zones, which may in turn decrease overall ethylene conversion and reduce residence time of the reaction mixture. It has been found that an optimized number of reaction zones can be accommodated by the use of cool ethylene sidestreams in lieu of long cooling zones and cooling zones may be shortened through the use of cold-jacketed reactor walls.

[0029] In the process of the invention, polymerization in the tubular reactor is carried out in at least five reaction zones, each reaction zone commencing at an initiator injection point. In each reaction zone, ethylene is converted to polymer, and therefore having a larger number of reaction zones generally increases conversion. However, each reaction zone will typically necessitate increasing the length of the tubular reactor and, therefore, will increase the pressure drop across the reactor. Advantageously, the initiator is injected at 5-7 different points along the tubular reactor thereby giving rise to 5-7 reaction zones. In one class of embodiments, the process has at least five reaction zones. In another class of embodiments the process has six or more reaction zones.

[0030] The function of the primary compressor is to pressurize fresh ethylene (make-up ethylene) to the pressure of the ethylene recycle system, for feed to the secondary compressor. The primary compressor may be a single compressor, that alone pressurizes the ethylene to the pressure of the recycle stream, or it may be two or more compressors in series or in parallel that, in combination, pressurize the fresh ethylene to the pressure of the ethylene recycle system. In some existing ethylene tubular reactor plants, the ethylene discharged from the primary compressor is divided into two streams, one stream being combined with recycled ethylene and fed to the suction of the secondary compressor, and the other stream being injected into the ethylene/polymer mixture downstream of the high-pressure, let-down valve, thereby providing rapid cooling of the ethylene/polymer mixture prior to entry into the product separation unit. In the process of the invention, preferably substantially the entire output of the primary compressor is fed to the secondary compressor.

[0031] Make-up ethylene is typically supplied to tubular reactor facilities at pressures from about 15 bar to 90 bar. Regardless of the ethylene supply pressure, in the process of the invention the primary compressor should have an ethylene gas throughput of at least 55 tonnes/hour. Preferably, the primary compressor operates at a gas throughput in the range of from 60 tonnes/hour to 120 tonnes/hour, more preferably in the range of from 70 tonnes/hour
to 110 tonnes/hour and especially preferably in the range of from 80 tonnes/hour to 100 tonnes/hour. As well as fresh make-up ethylene, the primary compressor may also receive ethylene recycled from the low pressure end of the product separator unit and from the primary and secondary compressor leakage systems.

[0032] It is also preferable to direct a small fraction of one of the ethylene recycle streams to a purge stream to limit build-up of inert components in the reactor system. In principle, the proportion of the total reactor gas throughput which is sent to the purge stream is typically in the range of from below 1% to 15%.

[0033] The discharge pressure of the primary compressor is matched to the pressure of the high pressure ethylene recycle system and may be, for example, in the range of from 270 bar to 350 bar, and is preferably in the range of from 280 bar to 320 bar. Also, the ethylene is preferably cooled after exit from the primary compressor and prior to entry into the secondary compressor.

[0034] The precise design of the primary compressor is not critical. However, in a favored embodiment, the primary compressor is a reciprocating compressor having at least 8 cylinders, preferably between 8 and 12 cylinders.

[0035] The secondary compressor compresses the ethylene to a pressure of at least 2000 bar for supply to the tubular reactor. As discussed with regard to the primary compressor, the secondary compressor is preferably a unit driven by a single motor, but may alternatively comprise two or more compressors in series or in parallel driven by separate motors. Any configuration of compressors, including the configuration described in greater detail below, is intended to be within the scope of this disclosure as long as said configuration is adapted to compress the ethylene from the intermediate pressure (of the ethylene as it leaves the primary compressor) to the desired reactor pressure in the range of 2000 bar to 2300 bar. The secondary compressor is mechanically complex and is subject to very high mechanical forces, but is nonetheless required to operate at a high throughput reliably and safely over a lifetime which may be several decades.

[0036] In one embodiment, the secondary compressor comprises a motor and a single compressor frame having multiple cylinders driven by the motor. The secondary compressor may be a two-stage reciprocating compressor having from six to sixteen or more cylinders, for example. It may be necessary to mount the compressor on foundations specially adapted to minimize vibration. Alternatively, the secondary compressor may comprise a motor and two cylinder frames arranged on opposite sides of the motor. In this embodiment, the cylinders may be smaller than where a single frame is used for comparable throughput. In
In this embodiment, the secondary compressor preferably has from 16 to 32 cylinders. Where the secondary compressor has two cylinder frames, one of the cylinder frames may be coupled to the motor via a flexible coupling. Whilst it is within the scope of the invention for each of the two frames to be connected to the motor via a flexible coupling, it is preferred to have only one coupled with a flexible coupling, the other compressor frame being coupled to the motor via a rigid coupling; rigid couplings being less costly and more robust than flexible couplings. Where the secondary compressor comprises two compressor frames, preferably one frame is dedicated to the first stage of compression and the other frame is dedicated to the second stage, thereby minimizing the complexity of the piping runs between stages.

The gas throughput through the secondary compressor is preferably in the range of about 160 tonnes/hour to 210 tonnes/hour, although higher throughputs may be warranted due to the desired low average reactor pressure.

The interstage pressure, that is, the pressure between the first and second stages of secondary compressor will typically be in the range of 1100 bar to 1600 bar. Upon leaving the secondary compressor, at least a portion of the ethylene passes to the front end of the tubular reactor. In a preferred embodiment, the ethylene discharged from the secondary compressor is divided into more than one stream, one of which enters the front end of the tubular reactor and the other or others enter as sidestreams at points along the length of the tubular reactor. In a particularly preferred embodiment, the ethylene discharged from the secondary compressor is split into 3-5 streams, with one stream going to the front end of the tubular reactor and the others entering as sidestreams. The streams may be of unequal volume, thereby providing flexibility in tailoring of the volume of ethylene entering each reaction zone in the tubular reactor.

In the process of polymerizing ethylene in a tubular reactor, once the desired throughput of ethylene through the secondary compressor and into the reactor is established, the pressure in the reactor is controlled by the high-pressure, let-down valve, through which the product mixture exits the reactor. Opening the valve decreases pressure in the tubular reactor; closing the valve increases the pressure. Moreover, a pressure drop exists along the length of the tubular reactor which forces the reaction mixture along the reactor at a desired velocity (the term "reactor pressure" herein refers to the maximum pressure in the reactor, that is, the pressure immediately downstream of the secondary compressor, unless another meaning is obvious from the context).

The secondary compressor compresses the ethylene to a sufficient pressure so as to keep the reaction mixture from undergoing phase separation until entering the high
pressure separator, but is otherwise minimized. In one embodiment, the pressure at the front end of the tubular reactor is in the range of from 2000 bar to 2500 bar, especially from 2000 bar to 2300 bar.

[0041] Alternatively, the pressure of the reactor may be determined such that the pressure at the back end of the tubular reactor is above the phase separation pressure of the reaction mixture for the reaction mixture’s given temperature, but not greater than 500 bar over the phase separation pressure. In this way, the pressure is kept as low as possible while still maintaining a substantially uniform gas phase throughout the reactor.

[0042] For example, an exemplary tubular reactor may have a pressure drop of from 300 bar to 500 bar, and preferably a pressure drop of about 400 bar. Moreover, the phase separation pressure of the reaction mixture depends on the specific contents of the reaction mixture itself, as well as the temperature of the reaction mixture. In one embodiment, the phase separation pressure of the reaction mixture at the back end of the tubular reactor may be between 1400 bar and 1600 bar, or about 1500 bar. With knowledge of the phase separation pressure and the tubular reactor’s pressure drop, the target pressure delivered from the secondary reactor may be determined. For example, with a phase separation pressure of about 1500 bar and a pressure drop across the reactor of about 400 bar, the pressure at the front end of the reactor may be determined to at least be 1900 bar and preferably at an adequately higher pressure, such as 2000 bar to allow for a margin of assurance that phase separation will not occur at the back end of the reactor.

[0043] Conversely, operation at high pressures, such as at pressures over 3100 bar, may enhance conversion, however, operation at such pressures typically results in ethylene polymer product with narrow MWD as well as other disadvantages such as increased loads on the secondary compressor, increased wall thickness of the tubular reactor, and increased length of the tubular reactor.

[0044] Ethylene is introduced into the front end of the tubular reactor and is heated to at least 95°C, preferably at least 135°C, and most preferably between 160°C and 200°C so that upon introduction of initiator, the initiator decomposes and the polymerization reaction begins. Polymerization commences immediately downstream of the initiator injection site thereby causing the temperature of the reaction mixture to rise due to the exothermic nature of the polymerization. As the temperature rises, initiator decomposition and polymerization increase in rate, accelerating the heat generation and causing the temperature to rise further. As initiator is consumed, initiation and polymerization slow and, at the point where heat
generation equals heat conducted away from the reaction mixture, the temperature peaks and then begins to fall.

[0045] Thus, as the reaction mixture travels along the length of the reactor, the temperature of the reaction mixture increases to a peak and then decreases until the next initiator injection point is reached, whereupon the process begins again. The zones downstream of initiator injection points in which the polymerization reaction occurs are known to the skilled person as reaction zones. The tubular reactor will generally be equipped with at least one temperature regulated heating/cooling jacket in each reaction zone.

[0046] In a class of embodiments in which ethylene discharge from the secondary compressor is split into more than one stream, with one stream entering the front end of the reactor and the other streams entering as sidestreams, each sidestream typically enters the reactor upstream of an initiator injection point, preferably after being cooled, for example, to between 10°C and 20°C, before entry into the reactor in order to reduce the temperature of the reaction mixture. As mentioned above, the total conversion of monomer to polymer along the length of the reactor is, in practice, limited by the ability to cool the reaction mixture, and so cooling the sidestreams can allow an increase in conversion for a given reactor as well as decrease the overall reactor length needed to adequately cool the reactor, thus limiting the necessary pressure drop across the reactor.

[0047] The increase in temperature in a reaction zone is proportional to the amount of polymer made in that reactor zone and so operating with high temperature deltas in each reaction zone favours high conversion. The kinetics of ethylene polymerization are such that as the temperature rises, chain transfer to polymer increases relative to propagation of linear chains and the polydispersity index increases. However, overly high peak temperatures may lead to ethylene decomposition. Thus, it is advantageous to operate with controlled peak temperatures and high temperature deltas in reaction zones, and particularly in the first reaction zones of the reactor.

[0048] Thus, in one preferable embodiment, upstream of an initiator injection point (i.e., in all but the last reaction zone) the reaction mixture is cooled to at least 50°C, more preferably to at least 60°C, and most preferably to at least 65°C, below the peak temperature of the previous reaction zone before the reaction mixture reaches the next initiator injection point. Preferably, the temperature immediately before each reaction zone is no greater than 240°C. The peak temperature for each reaction zone may advantageously be in the range of from 275°C to 350°C, and preferably no less than 280°C and no greater than 318°C. More preferably, the temperature immediately before each of the three most upstream reaction
zones in a reactor with five or more reaction zones is no greater than 220°C and the peak temperature for each of the three most upstream reaction zones is no lower than 300°C. Alternatively, the temperature immediately before each of the four most upstream reaction zones in a reactor with five or more reaction zones is no greater than 235°C and the peak temperature for each of the four most upstream reaction zones is no lower than 300°C.

[0049] The cooling in any reaction zone may be by means of a cooling jacket or a combination of a cooling jacket and introduction of a sidestream of cooled ethylene.

[0050] The proportion of the total ethylene which enters the tubular reactor, whether in the front end stream or as a sidestream, which is converted to polymer before exiting the reactor is referred to as the conversion. In the process of the invention, the conversion may be between 30-40% and preferably at least 35%. Conversions of higher than 40% are feasible but are not preferred, partly because the viscosity of the reaction mixture increases with its polymer content, which leads in turn to an increase in the pressure drop required to maintain the necessary flow velocity.

[0051] As mentioned above, the reactor pressure is controlled by operation of a high-pressure, let-down valve which is located at the downstream end of the tubular reactor. Whilst the flow exiting from the reactor could be divided into more than one stream with each stream passing through a respective high-pressure, let-down valve, in practice, it is preferred for there to be only one such valve, and for the entire output of the reactor to pass through it.

[0052] In a number of existing tubular reactor facilities, part of the ethylene discharge from the primary compressor is cooled and diverted in a separate stream to a location immediately downstream of the high-pressure, let-down valve (ethylene quench), to act as a rapid quench cooling of the product mixture. Preferably, however, all of the ethylene discharged from the primary compressor is conducted into the secondary compressor and subsequently into the tubular reactor, in order to maximize the amount of polymer produced and alternative means are provided for cooling the product mixture.

[0053] The combination of high throughput and the factors mentioned above relating to pressure drop over the length of the reactor make it undesirable in the process of the invention to provide more cooling capacity in the last reaction zone than is necessary to control the polymerization exotherm in the last reaction zone. Preferably, the temperature of the product mixture at the high-pressure, let-down valve is in the range of from 260°C to 290°C. Accordingly, downstream of the high-pressure, let-down valve and upstream of the product separator, further cooling means is provided, preferably in the form of a product
cooler comprising a conduit having a cooling jacket. From the product cooler the product mixture will typically flow directly into the first stage of the product separator unit.

[0054] Product separation may be carried out in a single stage. However, two stage separation is generally preferred. In the first stage, known as the high pressure separator, the first separation of polymer from unreacted ethylene is carried out. The separated gas is fed to the high pressure recycle system for return to the secondary compressor. The molten polymer in the bottom of the high pressure separator is decompressed into a second stage, known as a low pressure separator, and almost all of the remaining ethylene is separated from the polymer and is sent to the purge gas compression system. The polymer melt from the final stage of the product separator will typically be fed to one or more hot melt extruders, for combination with additives, extruding and pelletizing, as is conventional.

Product Properties

[0055] The process according to the invention results in an ethylene polymer product with a density of 0.910-0.930 g/cm³ (as measured by ASTM D1505) and a melt index between 0.1-20 dg/min (as measured by ASTM D1238). Preferably, the ethylene polymer obtained from the process according to the invention has a density of 0.915-0.920 g/cm³ and a melt index of 2-6 dg/min, and more preferably no less than 3 dg/min.

[0056] The ethylene polymer obtained from the process according to the invention has a polydispersity, Mw/Mn, of 1.0-50.0, preferably no less than 5.0, and more preferably no less than 7.0 measured using GPC (gel permeation chromatography) using following detectors: RI (refractive index) and LALS (low angle light scattering).

[0057] The ethylene polymer obtained from the process according to the invention exhibits a neck-in value of 2-8 cm, preferably no greater than 6 cm, and more preferably no greater than 5.00 cm, as measured at 295°C at 50 m/min and 25 rpm. Neck-in is measured on an extruded polymer web and is equal to W0-W1 where W0 = width of the extrusion die and W1 = width of the polymer web. The ethylene polymer also exhibits a draw down value of 100-1000 m/min, preferably no less than 125 m/min, and more preferably no less than 150 m/min as measured at 295°C at 10 m/min/sec. Draw down is the maximum line speed in m/min that a polymer web can withstand during extrusion before breaking down.

Homopolymerization

[0058] It is known in the art to manufacture ethylene copolymers by adding comonomers, such as methyl acrylate to the reaction mixture in addition to ethylene in order to produce copolymers with desired properties. However, the addition of such comonomers is governed by the availability on site of such comonomer and may require substantial investment cost
with regard to processing and storage equipment as well as high variable costs for some exotic or otherwise expensive comonomers. The process of the invention surprisingly results in a polymer with advantageous properties suitable for extrusion coating without the use of comonomers. Therefore, the process preferably results in a homopolymer.

**Modifier**

[0059] It is also an established practice to add modifier or chain transfer agent to control the molecular weight and melt index of a produced polymer. The process of the invention may involve the use of a modifier to control the molecular weight of the product polymer by promoting chain transfer. Examples of chain transfer agents include tetramethyldisilane, cyclopropane, sulfur hexafluoride, methane, t-butanol, perfluoropropane, deuterobenzene, ethane, ethylene oxide, 2,2-dimethylpropane, benzene, dimethyl sulfoxide, vinyl methyl ether, methanol, propane, 2-methyl-3-buten-2-ol, methyl acetate, t-butyl acetate, methyl formate, ethyl acetate, butane, triphenylphosphine, methylamine, methyl benzoate, ethyl benzoate, N,N-diisopropylacetamide, 2,2,4-trimethylpentane, n-hexane, isobutane, dimethoxymethane, ethanol, n-heptane, n-butyl acetate, cyclohexane, methylcyclohexane, 1,2-dichloroethane, acetonitrile, N-ethylacetamide, propylene, n-decane, N,N-diethylacetamide, cyclopentane, acetic anhydride, n-tridecane, n-butyl benzoate, isopropanol, toluene, hydrogen, acetone, 4,4-dimethylpentene-1, trimethylamine, N,N-dimethylacetamide, isobutylene, n-butyl isocyanate, methyl butyrate, n-butylamine, N,N-dimethylformamide, diethyl sulfide, diisobutylene, tetrahydrofuran, 4-methylpentene-1, p-xylene, p-dioxane, trimethylamine, butene-2, 1-bromo-2-chlorethane, octene-1, 2-methylbutene-2, cumene, butene-1, methyl vinyl sulfide, n-butynitrile, 2-methylbutene-1, ethylbenzene, n-hexadecene, 2-butanone, n-butyl isothiocyanate, methyl 3-cyanopropionate, tri-n-butylamine, 3-methyl-2-butanone, isobutyronitrile, di-n-butylamine, methyl chloroacetate, 3-methylbutene-1, 1,2-dibromoethane, dimethylamine, benzaldehyde, chloroform, 2-ethylhexene-1, propionaldehyde, 1,4 dichlorobutene-2, tri-n-butylphosphine, dimethylphosphine, methyl cyanocacetate, carbon tetrachloride, bromotrichloromethane, di-n-butylphosphine, acetaldehyde, and phosphine.

[0060] For further details of transfer agents, see Advances In Polymer Science, Vol. 7, pp. 386-448, (1970). Table 7 therein ranks several transfer agents in order of the chain transfer constant determined under set conditions. The tendency to copolymerize is indicated by the reactivity, also determined under set conditions.

[0061] The modifier can be added into the reaction mixture in any suitable way. For example, the modifier may be injected into the inlet pipes feeding one or more of the
secondary compressor first stage cylinders. The modifier is, in general, not fully consumed during one pass through the reactor and is generally also present in the recycled ethylene returning to the secondary compressor.

Initiators

[0062] Initiators are used to initiate the free radical ethylene polymerization and many suitable initiators will be known to the skilled person. Organic peroxide initiators are preferred. Typically, a blend of several initiators having different half-life temperatures will be used in order to achieve the desired reaction kinetics. Examples of suitable initiators include peresters including but not limited to bis(2 ethylhexyl)peroxydicarbonate, tert-Butyl per(2-ethyl)hexanoate, tert-Butyl perpivalate, tert-Butyl perneodecanoate, tert-Butyl perisobutyrate, tert-Butyl per-3,5,5,-trimethylhexanoate, tert-Butyl perbenzoate, and dialkyl peroxides including but not limited to di-tert-butyl peroxide.

[0063] The pure peroxides are mixed, typically in a hydrocarbon solvent, and are then injected into the tubular reactor at the initiator injection locations. Any suitable pump may be used, for example, a hydraulically driven piston pump.

[0064] The inventive process may advantageously use between 0.3 kg and 1.5 kg of initiator per tonne of polyethylene polymer produced, and preferably less than 0.7 kg of initiator per tonne of polyethylene.

Examples

[0065] An ethylene homopolymer was produced in a tubular reactor. The reactor had 5 reaction zones defined downstream of five initiator injection points. Ethylene was introduced to the front end of the reactor at 2300 bar, and through two sidestreams introduced before the second and third reaction zones. The pressure drop over the length of the reactor was 400 bar. Propionaldehyde and propylene were added as modifiers. The initiator added to the first reaction zone consisted of a mixture of organic peroxides including peroxybenzoate, peroxyoctoate, di-tert-butyl peroxide (DTBP), and peroxypropionate. The initiator added to the other 4 reaction zones consisted of a mixture of peroxybenzoate, peroxyoctoate, and DTBP. The polymerization temperature profile of the reaction mixture is summarized in Table 1. The resulting ethylene polymer properties including density, melt index, polydispersity, neck-in, and draw down were measured. These properties are summarized in Table 2.
The polymer of Example 1 compares favorably to other resins that are commercially available for extrusion coating applications. For example, the polymer of Example 1 is comparable to EXXONMOBIL™ LDPE LD 252 which has a density of 0.923 g/cm³ (ASTM D1505), melt index of 3.8 dg/min (ASTM D1238), and neck-in of 4.1 (315°C, 150 m/min), which is polymerized in an autoclave reactor.

With respect to the various ranges set forth herein, any upper limit recited may, of course, be combined with any lower limit for selected sub-ranges.

All patents and publications, including priority documents and testing procedures, referred to herein are hereby incorporated by reference in their entireties.

Although the methods and systems described herein and their advantages have been described in detail, it should be understood that various changes, substitutions, and alterations could be made without departing from the spirit and scope of the inventions described herein as defined by the following claims.

Table 1

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<th>Reaction Zone</th>
<th>Starting Temp. (°C)</th>
<th>Peak Temp. (°C)</th>
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<td>190</td>
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<td>285</td>
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Table 2

<table>
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<tr>
<th>Density</th>
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<tr>
<td>(g/cm³) (ASTM D1505)</td>
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<tr>
<td>Melt Index</td>
<td>3.6</td>
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<tr>
<td>(dg/min) (ASTM D1238)</td>
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<td>Mw/Mn (GPC)</td>
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<tr>
<td>Neck In</td>
<td>4.00</td>
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<tr>
<td>(cm) (295°C, 50 m/min)</td>
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<td>Draw Down</td>
<td>159</td>
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<td>(m/min) (295°C, 10 m/min/sec)</td>
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CLAIMS

What I Claimed Is:

1. A process for producing ethylene polymer comprising:
   compressing ethylene monomer in one or more compressors to a pressure between 2000 bar and 2300 bar;
   heating the ethylene monomer to a temperature between 135°C and 200°C;
   introducing the compressed, heated ethylene monomer into a front end of a tubular reactor;
   introducing initiator into the tubular reactor in at least five separate locations, thereby defining at least five reaction zones where the ethylene monomer polymerizes forming a reaction mixture comprising unreacted ethylene monomer and ethylene polymer; and
   separating the ethylene polymer from the reaction mixture;
   wherein the ethylene polymer has a polydispersity, Mw/Mn, no less than 5.0.

2. The process of claim 1, wherein the ethylene monomer or reaction mixture immediately upstream of the introduction of initiator in each of the at least five reaction zones has a temperature no greater than 240°C and the reaction mixture has a peak temperature no lower than 280°C in each of the at least five reaction zones.

3. The process of any one of the preceding claims, wherein the at least five reaction zones are oriented along the length of the tubular reactor from most upstream to most downstream, and
   wherein the ethylene monomer or reaction mixture immediately upstream of the introduction of initiator in each of the three most upstream reaction zones has a temperature no greater than 220°C and the reaction mixture has a peak temperature no lower than 300°C in each of the three most upstream reaction zones.

4. The process of any one of the preceding claims, wherein the at least five reaction zones are oriented along the length of the tubular reactor from most upstream to most downstream, and
   wherein the ethylene monomer or reaction mixture immediately upstream of the introduction of initiator in each of the four most upstream reaction zones has a temperature no greater than 235°C and the reaction mixture has a peak temperature no lower than 300°C in each of the four most upstream reaction zones.
5. The process of any one of the preceding claims, wherein the reaction mixture at a back end of the tubular reactor is at a pressure greater than its phase separation pressure for the reaction mixture’s given temperature but not greater than 500 bar above the phase separation pressure at the reaction mixture's given temperature.

6. The process of any one of the preceding claims, wherein no comonomer is introduced to the tubular reactor and the ethylene polymer is an ethylene homopolymer.

7. The process of any one of the preceding claims, wherein the tubular reactor comprises six or more reaction zones.

8. The process of any one of the preceding claims, wherein less than 1.5 kg of initiator is added to the reaction mixture per tonne of ethylene polymer produced.

9. The process of any one of the preceding claims, wherein the at least five reaction zones comprise first, second, third, fourth, and fifth reaction zones located from most upstream to most downstream in the tubular reactor, the process further comprising:
   introducing fresh ethylene, recycled ethylene, or both to the tubular reactor between the first and second reaction zones;
   introducing fresh ethylene, recycled ethylene, or both to the tubular reactor between the second and third reaction zones;
   introducing fresh ethylene, recycled ethylene, or both to the tubular reactor between the third and fourth reaction zones;
   cooling the reaction mixture between the fourth and fifth reaction zones without introducing additional ethylene to the tubular reactor; and
   cooling the reaction mixture between the fifth reaction zone and a high pressure let-down valve which terminates the tubular reactor without introducing additional ethylene to the tubular reactor.

10. The process of any one of the preceding claims, further comprising:
    producing an ethylene polymer exhibiting neck-in no greater than 5.00 cm measured at 295°C and 50 m/min, and draw down no less than 125 m/min determined at 295°C and 10 m/min/sec.
11. The process of any one of the preceding claims, further comprising:
producing an ethylene polymer with a melt index no less than 3 dg/min and density
between 0.915 g/cm³ and 0.920 g/cm³.

12. The process of any one of the preceding claims, further comprising:
producing an ethylene polymer with a polydispersity, Mw/Mn, no less than 7.0.

13. The process of any one of the preceding claims, further comprising:
releasing the reaction mixture through the high-pressure, let-down valve;
cooling the reaction mixture; and
separating the reaction mixture in a product separator into ethylene polymer and
unreacted ethylene;
wherein at least 30% of the ethylene monomer is converted to polymer.

14. The process of any one of the preceding claims, wherein the flow velocity in the
tubular reactor is in the range of from 14 to 20 m/s.

15. The process of any one of the preceding claims, wherein from 30% to 40% of the
ethylene monomer is converted to polymer.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IN V. C98 F2/01 C08F2/34 C08 L23/G4

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)
C08F C08 L

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

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* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another document or a special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"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
"Y" 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 novel or 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
"X" document member of the same patent family

Date of the actual completion of the international search: 9 June 2015
Date of mailing of the international search report: 30/06/2015

Name and mailing address of the ISA/
European Patent Office, P.O. 5818 Patentlaan 2 NL-2280 HV Rijswijk
Tel: (010) 390-2040, Fax: (010) 390-3016

Authorized officer:

Lux, Rudolf
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