



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 210/16, 2/34	A1	(11) International Publication Number: WO 98/52982 (43) International Publication Date: 26 November 1998 (26.11.98)
(21) International Application Number: PCT/US98/10253 (22) International Filing Date: 19 May 1998 (19.05.98) (30) Priority Data: 08/858,951 20 May 1997 (20.05.97) US (71) Applicant: UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US). (72) Inventors: KUPPERBLATT, Sandra, Ann; 8 Richard Drive, Flanders, NJ 07836 (US). EALER, George, Edward; 10 Lake Drive, Whitehouse Station, NJ 08889 (US). TILSTON, Michael, William; 2285 South Walnut Drive, St. Albans, WV 25177 (US). (74) Agent: JOHNSON WIGGINS, Karen; Union Carbide Chemicals & Plastics Technology Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).		(81) Designated States: AU, BR, CA, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: A PROCESS FOR PREPARING AN IN SITU POLYETHYLENE BLEND (57) Abstract <p>A process comprising contacting ethylene and one or two alpha-olefin comonomers, each having 3 to 8 carbon atoms, with a transition metal catalyst system including a hydrocarbylaluminum cocatalyst in each of two fluidized bed reactors connected in series, in the gas phase, under polymerization conditions. The copolymer formed in the first reactor has a flow index in the range of about 0.1 to about 75 grams per 10 minutes and a density in the range of 0.865 to 0.930 gram per cubic centimeter and the copolymer formed in the second reactor has a melt index in the range of about 0.2 to about 100 grams per 10 minutes and a density in the range of about 0.900 to about 0.965 gram per cubic centimeter, the weight ratio of the first reactor copolymer to second reactor copolymer being in the range of about 70:30 to about 30:70, and the in situ blend has a flow index in the range of about 5 to 100 grams per 10 minutes; a melt flow ratio in the range of about 10 about 100; a density in the range of 0.880 to 0.960 gram per cubic centimeter; and an Mw/Mn ratio in the range of about 2 to about 20.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

A PROCESS FOR PREPARING AN IN SITU POLYETHYLENE BLEND

Technical Field

This invention relates to a process for preparing an in situ polyethylene blend, which can be converted into film having a small number or essentially no gels (or fish-eyes).

Background Information

Polyethylenes of various densities have been prepared and converted into film characterized by excellent tensile strength, high ultimate elongation, good impact strength, and excellent puncture resistance. These properties together with toughness are enhanced when the polyethylene is of high molecular weight. However, as the molecular weight of the polyethylene increases, the processability of the resin usually decreases. By providing a blend of polymers of high molecular weight and low molecular weight, the properties characteristic of high molecular weight resins can be retained and processability, particularly extrudability (a characteristic of the lower molecular weight component) can be improved.

The blending of these polymers is successfully achieved in a staged reactor process similar to those described in United States patents 5,047,468 and 5,149,738. Briefly, the process is one for the in situ blending of polymers wherein a high molecular weight ethylene copolymer is prepared in one reactor and a low molecular weight ethylene copolymer is prepared in another reactor. The

- 2 -

process typically comprises continuously contacting, under polymerization conditions, a mixture of ethylene and one or more alpha-olefins with a catalyst system in two gas phase, fluidized bed reactors connected in series, said catalyst system comprising: (i) a supported magnesium/titanium based catalyst precursor; (ii) one or more aluminum containing activator compounds; and (iii) a hydrocarbyl aluminum cocatalyst,

While the in situ blends prepared as above and the films produced therefrom are found to have the advantageous characteristics heretofore mentioned, the commercial application of these granular broad molecular weight distribution polymers for high quality film applications is frequently limited by the level of gels obtained. Particle size distribution and flow characteristics studies indicate that the gas phase resins having an average particle size (APS) of about 400 to about 600 microns exhibit significant compositional, molecular, and rheological heterogeneities. When such a granular resin is compounded, for example, with conventional compounding equipment in a single pass, and the resulting pellets are fabricated into film, the film exhibits a high level of gels ranging in size from about 100 microns to about 500 microns. These gels adversely effect the aesthetic appearance, extrudability, and physical properties of the product. The gel characteristics of a film product are usually designated by a subjective scale of Film Appearance Rating (FAR) varying from minus 50 (very poor; these films have a large number of large gels) to plus 50 (very good; these films have a small amount of, or essentially no, gels). The FAR of the single pass film

- 3 -

product mentioned above is generally much worse than minus 50. For commercial acceptability, the FAR should be plus 20 or better.

Disclosure of the Invention

An object of this invention, therefore, is to provide a process for preparing an in situ blend, which can be extruded into a film having a commercially acceptable FAR. Other objects and advantages will become apparent hereinafter.

According to the present invention such a process has been discovered. The process comprises contacting ethylene and one or two alpha-olefin comonomers, each having 3 to 8 carbon atoms, with a transition metal catalyst system including a hydrocarbylaluminum cocatalyst in each of two fluidized bed reactors connected in series, in the gas phase, under polymerization conditions, with the provisos that:

(a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

(b) other than the active catalyst referred to in proviso (a), no additional catalyst is introduced into the second reactor;

(c) in the first reactor, in which a low density copolymer is made:

(1) alpha-olefin is present in a ratio of about 0.04 to about 1.48 moles of alpha-olefin per mole of ethylene;

(2) optionally, hydrogen is present in a ratio of about 0.01 to about 0.7 mole of hydrogen per mole of ethylene; and

- 4 -

(d) in the second reactor, in which a high density copolymer is made:

(1) alpha-olefin is present in a ratio of about 0.005 to about 0.8 mole of alpha-olefin per mole of ethylene;

(2) hydrogen is present in a ratio of about 0.01 to about 2.51 moles of hydrogen per mole of ethylene; and

(e) additional cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor

wherein the copolymer formed in the first reactor has a flow index in the range of about 0.1 to about 75 grams per 10 minutes and a density in the range of 0.865 to 0.930 gram per cubic centimeter and the copolymer formed in the second reactor has a melt index in the range of about 0.2 to about 100 grams per 10 minutes and a density in the range of about 0.900 to about 0.965 gram per cubic centimeter, the weight ratio of first reactor copolymer to second reactor copolymer being in the range of about 70:30 to about 30:70, and the in situ blend has a flow index in the range of about 5 to about 100 grams per 10 minutes; a melt flow ratio in the range of about 10 to about 100; a density in the range of 0.880 to 0.960 gram per cubic centimeter; and an Mw/Mn ratio in the range of about 2 to about 20; and

wherein the difference between the melt index-corrected density in the first reactor and the melt index-corrected density in the second reactor is no greater than 0.025 gram per cubic centimeter.

- 5 -

Description of the Preferred Embodiment(s)

The film is formed by extrusion. The extruder is a conventional one using a die, which will provide the desired gauge. The gauge of the films of interest here can be in the range of about 0.3 to about 2.5 mils, and is preferably in the range of about 0.75 to about 2 mils.

Examples of various extruders, which can be used in forming the film, are the single screw type modified with a blown film die and air ring and continuous take off equipment. A typical single screw type extruder can be described as one having a hopper at its upstream end and a die at its downstream end. The hopper feeds into a barrel, which contains a screw. At the downstream end, between the end of the screw and the die, is a screen pack and a breaker plate. The screw portion of the extruder is considered to be divided up into three sections, the feed section, the compression section, and the metering section, and multiple heating zones from the rear heating zone to the front heating zone, the multiple sections and zones running from upstream to downstream. If it has more than one barrel, the barrels are connected in series. The length to diameter ratio of each barrel is in the range of about 16:1 to about 30:1. The extrusion can take place at temperatures in the range of about 160 to about 270 degrees C, and is preferably carried out at temperatures in the range of about 180 to about 240 degrees C.

The blend is produced in two staged reactors connected in series wherein a mixture of resin and active catalyst is transferred from the first reactor to the second reactor in which another

- 6 -

copolymer is prepared and blends in situ with the copolymer from the first reactor. The term "two ... reactors" can mean two independent reactors or two stages in one reactor. The first reactor is the low density reactor and the second reactor is the high density reactor. The reactor is named according to the relative density of the polymer produced in the reactor.

The copolymers produced in each of the reactors are copolymers of ethylene and one or two alpha-olefin comonomers, each having 3 to 8 carbon atoms, and can be, for example, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. It will be understood that the term copolymers includes terpolymers. It is preferred that the comonomers be the same in each reactor; however, different comonomers can be used in each reactor, if desired. The preferred comonomers are 1-butene and 1-hexene.

For a staged reactor system, the proportions of the low and high density components are controlled via the relative production rate in each reactor. The relative production rate in each reactor can, in turn, be controlled by a computer application program, which monitors the production rate in the reactors (measured by heat balance) and then manipulates the ethylene partial pressure in each reactor and catalyst feed rate in order to meet the production rate, the production rate split, and catalyst productivity requirements.

Various transition metal catalyst systems can be used to effect the polymerization, which is carried out in the reactors. The in situ polyethylene blend of subject invention is preferably produced in the gas phase by various low pressure processes. The blend can also be produced in the liquid phase in solutions or slurries by

- 7 -

conventional techniques, again at low pressures. Low pressure processes are typically run at pressures below 1000 psi whereas high pressure processes are typically run at pressures above 15,000 psi. Typical transition metal catalyst systems, which can be used to prepare the in situ blend, are magnesium/titanium based catalyst systems, which can be exemplified by the catalyst system described in United States patent 4,302,565; vanadium based catalyst systems such as those described in United States patents 4,508,842; 5,332,793; 5,342,907; and 5,410,003; a chromium based catalyst system such as that described in United States patent 4,101,445; and a metallocene based catalyst system including an aluminoxane cocatalyst such as those described in United States patents 4,937,299; 5,317,036; and 5,527,752. Many of these catalyst systems are often referred to as Ziegler-Natta catalyst systems. Catalyst systems, which use chromium or molybdenum oxides on silica-alumina supports, are also useful. Typical processes for preparing in situ polyethylene blends are described in United States Patents 5,371,145 and 5,405,901. Preferred catalyst systems for preparing the in situ blends of this invention are magnesium/titanium catalyst systems and metallocene catalyst systems.

The magnesium/titanium based catalyst system will be used to exemplify the in situ process, e.g., the catalyst system described in United States patent 4,302,565 although the precursor is preferably unsupported and another catalyst system in which the precursor is formed by spray drying and is used in slurry form. Such a catalyst precursor, for example, contains titanium, magnesium, an electron donor, and, optionally, an aluminum halide. The precursor is

- 8 -

then introduced into a hydrocarbon medium such as mineral oil to provide the slurry form. This catalyst system is described in United States patent 5,290,745.

The electron donor, if used in the catalyst precursor, is an organic Lewis base, liquid at temperatures in the range of about 0 degrees C to about 200 degrees C, in which the magnesium and titanium compounds are soluble. The electron donor can be an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ketone, an aliphatic amine, an aliphatic alcohol, an alkyl or cycloalkyl ether, or mixtures thereof, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donor is tetrahydrofuran. Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate.

While an excess of electron donor is used initially to provide the reaction product of titanium compound and electron donor, the reaction product finally contains about 1 to about 20 moles of electron donor per mole of titanium compound and preferably about 1 to about 10 moles of electron donor per mole of titanium compound.

An activator compound, which is generally used with any of the titanium based catalyst precursors, can have the formula

- 9 -

$AlR_aX_bH_c$ wherein each X is independently chlorine, bromine, iodine, or OR'; each R and R' is independently a saturated aliphatic hydrocarbon radical having 1 to 14 carbon atoms; b is 0 to 1.5; c is 0 or 1; and $a+b+c = 3$. Preferred activators include alkylaluminum mono- and dichlorides wherein each alkyl radical has 1 to 6 carbon atoms and the trialkylaluminums. Examples are diethylaluminum chloride and tri-n-hexylaluminum. About 0.10 to about 10 moles, and preferably about 0.15 to about 2.5 moles, of activator are used per mole of electron donor. The molar ratio of activator to titanium is in the range of about 1:1 to about 10:1, and is preferably in the range of about 2:1 to about 5:1.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R_3Al or R_2AlX wherein each R is independently alkyl, cycloalkyl, aryl, or hydrogen; at least one R is hydrocarbyl; and two or three R radicals can be joined to form a heterocyclic structure. Each R, which is a hydrocarbyl radical, can have 1 to 20 carbon atoms, and preferably has 1 to 10 carbon atoms. X is a halogen, preferably chlorine, bromine, or iodine. Examples of hydrocarbyl aluminum compounds are as follows:

triisobutylaluminum, tri-n-hexylaluminum, di-isobutyl-aluminum hydride, dihexylaluminum hydride, di-isobutyl-hexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum, tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, tritolylaluminum, dibutylaluminum chloride, diethylaluminum

- 10 -

chloride, and ethylaluminum sesquichloride. The cocatalyst compounds can also serve as activators and modifiers.

As noted above, it is preferred not to use a support. However, in those cases where it is desired to support the precursor, silica is the preferred support. Other suitable supports are inorganic oxides such as aluminum phosphate, alumina, silica/alumina mixtures, silica modified with an organoaluminum compound such as triethylaluminum, and silica modified with diethyl zinc. A typical support is a solid, particulate, porous material essentially inert to the polymerization. It is used as a dry powder having an average particle size of about 10 to about 250 microns and preferably about 30 to about 100 microns; a surface area of at least 200 square meters per gram and preferably at least about 250 square meters per gram; and a pore size of at least about 100 angstroms and preferably at least about 200 angstroms. Generally, the amount of support used is that which will provide about 0.1 to about 1.0 millimole of titanium per gram of support and preferably about 0.4 to about 0.9 millimole of titanium per gram of support. Impregnation of the above mentioned catalyst precursor into a silica support can be accomplished by mixing the precursor and silica gel in the electron donor solvent or other solvent followed by solvent removal under reduced pressure. When a support is not desired, the catalyst precursor can be used in liquid form.

Activators can be added to the precursor either before and/or during polymerization. In one procedure, the precursor is fully activated before polymerization. In another procedure, the precursor is partially activated before polymerization, and activation is

- 11 -

completed in the reactor. Where a modifier is used instead of an activator, the modifiers are usually dissolved in an organic solvent such as isopentane and, where a support is used, impregnated into the support following impregnation of the titanium compound or complex, after which the supported catalyst precursor is dried. Otherwise, the modifier solution is added by itself directly to the reactor. Modifiers are similar in chemical structure and function to the activators as are cocatalysts. For variations, see, for example, United States patent 5,106,926. The cocatalyst is preferably added separately neat or as a solution in an inert solvent, such as isopentane, to the polymerization reactor at the same time as the flow of ethylene is initiated.

United States patent 5,106,926 provides another example of a magnesium/titanium based catalyst system comprising:

(a) a catalyst precursor having the formula

$Mg_dTi(OR)_eX_f(ED)_g$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is a aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is the same or different; X is independently chlorine, bromine or iodine; ED is an electron donor; d is 0.5 to 56; e is 0, 1, or 2; f is 2 to 116; and g is $1.5d+2$;

(b) at least one modifier having the formula BX_3 or $AlR_{(3-e)}X_e$ wherein each R is alkyl or aryl and is the same or different, and X and e are as defined above for component (a)

wherein components (a) and (b) are impregnated into an inorganic support; and

- 12 -

(c) a hydrocarbyl aluminum cocatalyst.

The precursor is prepared from a titanium compound, a magnesium compound, and an electron donor. Titanium compounds, which are useful in preparing these precursors, have the formula $\text{Ti(OR)}_e\text{X}_h$ wherein R, X, and e are as defined above for component (a); h is an integer from 1 to 4; and e+h is 3 or 4. Examples of titanium compounds are TiCl_3 , TiCl_4 , $\text{Ti(OC}_2\text{H}_5)_2\text{Br}_2$, $\text{Ti(OC}_6\text{H}_5)_3\text{Cl}_3$, $\text{Ti(OCOCH}_3)_3\text{Cl}_3$, and $\text{Ti(OCOC}_6\text{H}_5)_3\text{Cl}_3$. The magnesium compounds include magnesium halides such as MgCl_2 , MgBr_2 , and MgI_2 . Anhydrous MgCl_2 is a preferred compound. About 0.5 to 56, and preferably about 1 to 10, moles of the magnesium compounds are used per mole of titanium compound.

The electron donor, the support, and the cocatalyst are the same as those described above. As noted, the modifier can be similar in chemical structure to the aluminum containing activators. The modifier has the formula BX_3 or $\text{AlR}_{(3-e)}\text{X}_e$ wherein each R is independently alkyl having 1 to 14 carbon atoms; each X is independently chlorine, bromine, or iodine; and e is 1 or 2. One or more modifiers can be used. Preferred modifiers include alkylaluminum mono- and dichlorides wherein each alkyl radical has 1 to 6 carbon atoms; boron trichloride; and the trialkylaluminums. About 0.1 to about 10 moles, and preferably about 0.2 to about 2.5 moles, of modifier can be used per mole of electron donor. The molar ratio of modifier to titanium can be in the range of about 1:1 to about 10:1 and is preferably in the range of about 2:1 to about 5:1.

- 13 -

The entire catalyst system, which includes the precursor or activated precursor and the cocatalyst, is added to the first reactor. The catalyst is admixed with the copolymer produced in the first reactor, and the mixture is transferred to the second reactor. Insofar as the catalyst is concerned, only cocatalyst is added to the second reactor from an outside source.

The polymerization in each reactor is, preferably, conducted in the gas phase using a continuous fluidized process. A typical fluidized bed reactor is described in United States patent 4,482,687.

A relatively low density copolymer is prepared in the first reactor and the relatively high density copolymer in the second reactor.

The first reactor is generally smaller in size than the second reactor because only a portion of the final product is made in the first reactor. The mixture of polymer and an active catalyst is usually transferred from the first reactor to the second reactor via an interconnecting device using nitrogen or second reactor recycle gas as a transfer medium.

In the low density reactor:

The flow index can be in the range of about 0.1 to about 75 grams per 10 minutes, and is preferably in the range of about 1 to about 30 grams per 10 minutes. The molecular weight of this polymer is, generally, in the range of about 89,000 to about 490,000. The density of the copolymer can be in the range of 0.865 to 0.930 gram per cubic centimeter, and is preferably in the range of 0.880 to 0.920 gram per cubic centimeter. The melt flow ratio of the polymer

- 14 -

can be in the range of about 10 to about 50, and is preferably about 12 to about 40.

Melt index is determined under ASTM D-1238, Condition E. It is measured at 190 degrees C and 2.16 kilograms and reported as grams per 10 minutes. Flow index is determined under ASTM D-1238, Condition F. It is measured at 190 degrees C and 10 times the weight used in determining the melt index, and reported as grams per 10 minutes. Melt flow ratio is the ratio of flow index to melt index.

In the high density reactor:

A relatively high density copolymer is prepared in this reactor. The melt index can be in the range of about 0.2 to about 100 grams per 10 minutes, and is preferably in the range of about 0.4 to about 90 grams per 10 minutes. The molecular weight of the high density copolymer is, generally, in the range of about 31,000 to about 164,000. The density of the copolymer prepared in this reactor can be in the range of 0.900 to 0.965 gram per cubic centimeter, and is preferably in the range of 0.910 to 0.960 gram per cubic centimeter. The melt flow ratio of this copolymer can be in the range of about 10 to about 40, and is preferably about 12 to about 35.

The blend or final product, as removed from the second reactor, can have a flow index in the range of about 5 to about 100 grams per 10 minutes, and preferably has a flow index in the range of about 7 to about 80 grams per 10 minutes. The molecular weight of the final product is, generally, in the range of about 150,000 to about 350,000. The density of the blend can be in the range of 0.880 to 0.960 gram per cubic centimeter, and is preferably in the range of

- 15 -

0.900 to 0.955 gram per cubic centimeter. The melt flow ratio of the blend can be in the range of about 10 to about 100, and is preferably in the range of about 12 to about 70.

Insofar as the densities in the low density (first) reactor and the high density (second) reactor are concerned, they are limited in that the difference in melt index-corrected densities between the copolymers prepared in each reactor is no greater than 0.025 gram per cubic centimeter, and is preferably no greater than 0.022 gram per cubic centimeter. Melt index-corrected density is defined below.

The blend can have an Mw/Mn ratio of about 2 to about 20, and preferably has an Mw/Mn ratio of about 3 to about 15. Mw is the weight average molecular weight; Mn is the number average molecular weight; and the Mw/Mn ratio can be referred to as the polydispersity index, which is a measure of the breadth of the molecular weight distribution. When the term "molecular weight" is used by itself, it means weight average molecular weight.

The weight ratio of copolymer prepared in the low density reactor to the copolymer prepared in the high density reactor can be in the range of about 70:30 to about 30:70.

The catalyst system, ethylene, alpha-olefin, and, optionally, hydrogen are continuously fed into the first reactor; the polymer/catalyst mixture is continuously transferred from the first reactor to the second reactor; ethylene, alpha-olefin, and hydrogen, as well as cocatalyst are continuously fed to the second reactor. The final product is continuously removed from the second reactor.

In the low density reactor:

- 16 -

The mole ratio of alpha-olefin to ethylene can be in the range of about 0.04:1 to about 1.48:1, and is preferably in the range of about 0.09:1 to about 1.04:1. The mole ratio of hydrogen (if used) to ethylene can be in the range of about 0.01:1 to about 0.7:1, and is preferably in the range of about 0.01:1 to about 0.5:1. The operating temperature is generally in the range of about 60 degrees C to about 100 degrees C. Preferred operating temperatures vary depending on the density desired, i.e., lower temperatures for lower densities and higher temperatures for higher densities.

In the high density reactor:

The mole ratio of alpha-olefin to ethylene can be in the range of about 0.005:1 to about 0.8:1, and is preferably in the range of about 0.005:1 to about 0.6:1. The mole ratio of hydrogen to ethylene can be in the range of about 0.01:1 to about 2.51:1, and is preferably in the range of about 0.01:1 to about 2.41:1. The operating temperature is generally in the range of about 70 degrees C to about 100 degrees C. As mentioned above, the temperature is preferably varied with the desired density.

The pressure is generally the same in both the first and second reactors. The pressure can be in the range of about 200 to about 450 psig and is preferably in the range of about 280 to about 350 psig.

A typical fluidized bed reactor can be described as follows:

The bed is usually made up of the same granular resin that is to be produced in the reactor. Thus, during the course of the polymerization, the bed comprises formed polymer particles, growing

- 17 -

polymer particles, and catalyst particles fluidized by polymerization and modifying gaseous components introduced at a flow rate or velocity sufficient to cause the particles to separate and act as a fluid. The fluidizing gas is made up of the initial feed, make-up feed, and cycle (recycle) gas, i.e., comonomers and, if desired, modifiers and/or an inert carrier gas.

The essential parts of the reaction system are the vessel, the bed, the gas distribution plate, inlet and outlet piping, a compressor, cycle gas cooler, and a product discharge system. In the vessel, above the bed, there is a velocity reduction zone, and, in the bed, a reaction zone. Both are above the gas distribution plate.

Conventional additives, which can be introduced into the blend, are exemplified by antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents, crosslinking agents, catalysts, and boosters, tackifiers, and anti-blocking agents. Aside from the fillers, the additives can be present in the blend in amounts of about 0.1 to about 10 parts by weight of additive for each 100 parts by weight of polymer blend. Fillers can be added in amounts of up to 200 parts by weight and more for each 100 parts by weight of the blend.

An advantage of the film prepared from the in situ blend of this invention is an FAR of at least plus 30 under high and low shear compounding conditions..

Patents mentioned in this specification are incorporated by reference herein.

- 18 -

The invention is illustrated by the following examples.

Examples 1 and 2

Example 1 is an embodiment of the invention showing the narrow density difference and higher FAR, and example 2 is a comparative example showing a greater density difference and lower FAR.

The preferred catalyst system is one where the precursor is formed by spray drying and is used in slurry form. Such a catalyst precursor, for example, contains titanium, magnesium, aluminum halides, and an electron donor. The precursor is then introduced into a hydrocarbon medium such as mineral oil to provide the slurry form. See United States patent 5,290,745 (' 745). The catalyst composition and method of preparing same used in this example is of the same composition and preparation method as example 1 of ' 745 except that 0.45 mol of diethylaluminum chloride per mol of tetrahydrofuran is used instead of 0.5 mol.

Polyethylene is produced using the following standard procedure.

Ethylene is copolymerized with 1-hexene in each reactor. Trimethylaluminum (TMA) cocatalyst is added to each reactor during polymerization as a 2 weight percent solution in isopentane in the first reactor and a 1 weight percent solution in isopentane in the second reactor. The temperature in the first reactor is 70 degrees C and the temperature in the second reactor is 80 degrees C. The pressure in each reactor is 300 pounds per square inch absolute (psia).

- 19 -

Each polymerization is continuously conducted after equilibrium is reached under the conditions set forth here and in Tables I and II.

Polymerization is initiated in the first reactor by continuously feeding the above catalyst precursor and cocatalyst into a fluidized bed of polyethylene granules together with ethylene, 1-hexene, and hydrogen. The resulting copolymer mixed with active catalyst is withdrawn from the first reactor and transferred to the second reactor using nitrogen as a transfer medium. The second reactor also contains a fluidized bed of polyethylene granules. Again, ethylene, 1-hexene, and hydrogen are introduced into the second reactor where they come into contact with the copolymer and catalyst from the first reactor. Additional cocatalyst is also introduced. The product blend is continuously removed. It is compounded in a Banbury™ mixer at 100 revolutions per minute (rpm) for 90 seconds using a 20 mesh screen.

Variable polymerization conditions, resin properties, film extrusion conditions, and film properties for example 1 are set forth in Table I and for comparative example 2 in Table II.

All molecular weights in this specification are weight average molecular weights unless otherwise designated.

- 20 -

Table I

Polymerization conditions	first reactor	second reactor
C2 partial pressure (psia)	35	85
H2/C2 molar ratio	0.082	0.860
C6/C2 molar ratio	0.12	0.1
Catalyst feeder (rpm)	7000	-----
TMA feed rate (cc/hr)	120	115
C2 feed (lbs/hr)	21	25
Total production rate (lbs/hr)	-----	57
Bed weight(lbs)	80	120
Residence time (hrs)	3.2	2.1
Recycle isopentane (mol %)	11	2.2
Al/Ti molar ratio	22	25
Titanium split (weight %)	0.492	0.508
Computer indicated split (weight %)	0.49	0.51

- 21 -

Table I (continued)

Resin properties	first reactor	second reactor	final product
Flow index (g/10 min)	1.5	-----	19
Melt index (g/10 min)	-----	16.0	0.45
Density(g/cc)	0.915	0.940	0.928
Melt index- corrected density(g/cc)	0.921	0.934	-----
Melt flow ratio	-----	-----	41
Residual aluminum(ppm)	70	-----	42
Residual titanium(ppm)	5.9	-----	2.9
Bulk density (lbs/cu ft)	22.2	-----	24
Average particle size(inch)	0.015	-----	0.017
finer: less than 120 mesh (wt %)	5	-----	3
Mw/Mn	5.2	-----	6.0
Film extrusion conditions:			

- 22 -

Melt temperature (degrees C)	-----	-----	240
Die rate(lbs/hr/in)	-----	-----	3.6
Frostline height (inches)	-----	-----	7
Blow up ratio	-----	-----	2.5:1
Gauge(mil)	-----	-----	1
Film properties: FAR			
Higher shear compounding	-----	-----	plus 40
Lower shear compounding	-----	-----	plus 40

- 23 -

Table II

Polymerization conditions	first reactor	second reactor
C2 partial pressure (psia)	30	102
H2/C2 molar ratio	0.045	0.910
C6/C2 molar ratio	0.18	0.03
Catalyst feeder (rpm)	10,000	-----
TMA feed rate (cc/hr)	95	100
C2 feed (lbs/hr)	19.5	28
Total production rate (lbs/hr)	-----	56
Bed weight(lbs)	80	125
Residence time (hrs)	3.2	2.2
Recycle isopentane (mol %)	9	12.3
Al/Ti molar ratio	20	30
Titanium split (weight %)	0.438	0.563
Computer indicated split (weight %)	0.45	0.55

- 24 -

Table II (continued)

Resin properties	first reactor	second reactor	final product
Flow index (g/10 min)	1.8	-----	18
Melt index (g/10 min)	-----	16.0	0.43
Density(g/cc)	0.902	0.950	0.929
Melt index- corrected density (g/cc)	0.907	0.944	-----
Melt flow ratio	-----	-----	41.9
Residual aluminum(ppm)	54	-----	36
Residual titanium(ppm)	4.8	-----	2.1
Bulk density (lbs/cu ft)	21.5	-----	23
Average particle size(inch)	0.018	-----	0.022
Fines: less than 120 mesh (wt %)	0.5	-----	0.31
Mw/Mn	-----	-----	5.4

- 25 -

Table II (continued)**Film extrusion
conditions:**

Melt temperature (degrees C)	-----	-----	246
Die rate(lbs/hr/in)	-----	-----	3.6
Frostline height (inches)	-----	-----	7
Blow up ratio	-----	-----	2.5:1
Gauge(mil)	-----	-----	1

Film properties:**FAR**

Higher shear compounding	-----	-----	plus 10
Lower shear compounding	-----	-----	0

Notes to above Tables:

1. Resin properties for second reactor: these are theoretical values based on the assumption that the second reactor copolymer is produced independently.
2. The films are extruded in a 1.5 inch Old Sterling™ blown tubular film extruder having a length to diameter ratio of 24:1;

- 26 -

a linear low density polyethylene screw; a 3 inch die; and a die gap of 70 mils.

3. FAR is determined as follows: A 78 inch by 12 inch section of film is visually analyzed for gels (fish-eyes) taking into account the size and number present. This is compared against internal standards, which are rated in 10 unit increments from minus 50 to plus 50. The closest standard to the actual film section is then the rating that is given to the film.

4. Density is measured by producing a plaque in accordance with ASTM D-1928, procedure C, and then testing as is via ASTM D-1505.

5. Melt flow ratio is the ratio of flow index to melt index.

6. The molecular weight and molecular weight distribution (polydispersity) are determined via Size Exclusion Chromatography (SEC) using a Waters™ 150C GPC instrument at 140 degrees C with 1,2,4- trichlorobenzene as solvent at a flow rate of 1 milliliter per minute. The pore size range of the column set provides for a molecular weight separation covering 200 to 10,000,000 Daltons. National Institute of Standards Technology polyethylene standard NBS1475 is used as the broad standard calibrant to obtain the molecular weight distribution.

7. Die rate is defined as pounds per hour per inch of die circumference.

8. Frostline height is that distance off of the base of the die during which the polymer undergoes a phase transformation from a viscous liquid to a solid.

- 27 -

9. Blow up ratio is the ratio of the bubble diameter to the die diameter.

10. Melt index-corrected density is defined as follows: It is the density of a polymer, which, with respect to the polymer in the reactor, has the same weight percent of comonomer incorporation, the same comonomer, and a melt index of 1.0 gram per 10 minutes. The melt-corrected density of the polymer in the reactor is determined by using the following equation:

Melt index-corrected density (g/cc) = density (g/cc) minus 0.002 times the natural logarithm of the melt index (g/10 min).

For example, a polymer having a flow index of 1.0 gram per 10 minutes; a melt index of 0.036 gram per 10 minutes; and a density of 0.900 gram per cubic centimeter has a melt index-corrected density of 0.9067 gram per cubic centimeter.

- 28 -

Claims

1. A process comprising contacting ethylene and one or two alpha-olefin comonomers, each having 3 to 8 carbon atoms, with a transition metal catalyst system including a hydrocarbylaluminum cocatalyst in each of two fluidized bed reactors connected in series, in the gas phase, under polymerization conditions, with the provisos that:

(a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

(b) other than the active catalyst referred to in proviso (a), no additional catalyst is introduced into the second reactor;

(c) in the first reactor, in which a low density copolymer is made:

(1) alpha-olefin is present in a ratio of about 0.04 to about 1.48 moles of alpha-olefin per mole of ethylene;

(2) optionally, hydrogen is present in a ratio of about 0.01 to about 0.7 mole of hydrogen per mole of ethylene; and

(d) in the second reactor, in which a high density copolymer is made:

(1) alpha-olefin is present in a ratio of about 0.005 to about 0.8 mole of alpha-olefin per mole of ethylene;

(2) hydrogen is present in a ratio of about 0.01 to about 2.51 moles of hydrogen per mole of ethylene; and

- 29 -

(e) additional cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor

wherein the copolymer formed in the first reactor has a flow index in the range of about 0.1 to about 75 grams per 10 minutes and a density in the range of 0.865 to 0.930 gram per cubic centimeter and the copolymer formed in the second reactor has a melt index in the range of about 0.2 to about 100 grams per 10 minutes and a density in the range of about 0.900 to about 0.965 gram per cubic centimeter, the weight ratio of first reactor copolymer to second reactor copolymer being in the range of about 70:30 to about 30:70, and the in situ blend has a flow index in the range of about 5 to about 100 grams per 10 minutes; a melt flow ratio in the range of about 10 to about 100; a density in the range of 0.880 to 0.960 gram per cubic centimeter; and an Mw/Mn ratio in the range of about 2 to about 20; and

wherein the difference between the melt index-corrected density in the first reactor and the melt index-corrected density in the second reactor is no greater than 0.025 gram per cubic centimeter.

2. The process defined in claim 1 wherein the blend has a flow index in the range of about 7 to about 80 grams per 10 minutes; a melt flow ratio in the range of about 12 to about 70; a density in the range of 0.900 to 0.955 gram per cubic centimeter; and an Mw/Mn ratio in the range of about 3 to about 15.

- 30 -

3. The process defined in claim 1 wherein, in the first reactor, the copolymer has a flow index in the range of about 1 to about 30 grams per 10 minutes and a density in the range of 0.880 to 0.920 gram per cubic centimeter, and, in the second reactor, the copolymer has a melt index in the range of about 0.4 to about 90 grams per 10 minutes and a density in the range of 0.910 to 0.960 gram per cubic centimeter, and wherein the difference between the melt index-corrected density in the first reactor and the melt index-corrected density in the second reactor is no greater than 0.022 gram per cubic centimeter.

4. The process defined in claim 1 wherein the alpha-olefin(s) are the same in each reactor.

5. The process defined in claim 1 wherein the alpha-olefin(s) are 1-butene and/or 1-hexene.

6. The process defined in claim 1 wherein, in the first reactor, the mole ratio of alpha-olefin to ethylene is in the range of about 0.09:1 to about 1.04:1 and the mole ratio of hydrogen, which is optional, to ethylene is in the range of about 0.01:1 to about 0.5:1, and, in the second reactor, the mole ratio of alpha-olefin to ethylene is in the range of about 0.005:1 to about 0.6:1 and the mole ratio of hydrogen to ethylene is in the range of about 0.01:1 to about 2.41:1.

- 31 -

7. A process comprising contacting ethylene and one or two α -olefin comonomers, each having 3 to 8 carbon atoms, with a transition metal catalyst system including a hydrocarbylaluminum cocatalyst in each of two fluidized bed reactors connected in series, in the gas phase, under polymerization conditions, with the provisos that:

(a) the mixture of ethylene copolymer matrix and active catalyst formed in the first reactor in the series is transferred to the second reactor in the series;

(b) other than the active catalyst referred to in proviso (a), no additional catalyst is introduced into the second reactor;

(c) in the first reactor, in which a low density copolymer is made:

(1) α -olefin is present in a ratio of about 0.09 to about 1.04 moles of α -olefin per mole of ethylene;

(2) hydrogen is present in a ratio of about 0.01 to about 0.5 mole of hydrogen per mole of ethylene; and

(d) in the second reactor, in which a high density copolymer is made:

(1) α -olefin(s) are the same as the α -olefin(s) in the first reactor and are present in a ratio of about 0.005 to about 0.6 mole of α -olefin per mole of ethylene;

(2) hydrogen is present in a ratio of about 0.01 to about 2.41 moles of hydrogen per mole of ethylene; and

- 32 -

(e) additional cocatalyst is introduced into the second reactor in an amount sufficient to restore the level of activity of the catalyst transferred from the first reactor to about the initial level of activity in the first reactor

wherein the copolymer formed in the first reactor has a flow index in the range of about 1 to about 30 grams per 10 minutes and a density in the range of 0.880 to 0.920 gram per cubic centimeter and the copolymer formed in the second reactor has a melt index in the range of about 0.4 to about 90 grams per 10 minutes and a density in the range of about 0.910 to about 0.960 gram per cubic centimeter, the weight ratio of first reactor copolymer to second reactor copolymer being in the range of about 70:30 to about 30:70, and the in situ blend has a flow index in the range of about 7 to about 80 grams per 10 minutes; a melt flow ratio in the range of about 12 to about 70; a density in the range of 0.900 to 0.955 gram per cubic centimeter; and an Mw/Mn ratio in the range of about 3 to about 15; and

wherein the difference between the melt index-corrected density in the first reactor and the melt index-corrected density in the second reactor is no greater than 0.022 gram per cubic centimeter.

8. The process defined in claim 1 wherein the catalyst system is a metallocene catalyst system including an aluminoxane cocatalyst.

- 33 -

9. The process defined in claim 6 wherein the catalyst system is a metallocene catalyst system including an aluminoxane cocatalyst.

10. A film extruded from the in situ blend prepared by the process defined in claim 6 having an FAR of at least plus 30.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/10253

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F210/16 C08F2/34

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)

IPC 6 C08F

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 691 367 A (UNION CARBIDE CHEM PLASTIC) 10 January 1996 see example 5; table 5 see claims 1,3-6 ---	1-7,10
X	EP 0 754 708 A (UNION CARBIDE CHEM PLASTIC) 22 January 1997 see column 14, line 52 - column 15, line 40 see column 16, line 18 - line 24 see claims 1,4-8 ---	1-7,10
P,X	EP 0 794 200 A (UNION CARBIDE CHEM PLASTIC) 10 September 1997 see claims 1-8 see examples 1-6 see page 7, line 17 - line 20 --- -/--	1-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° 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 document 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 citation or other 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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

27 August 1998

Date of mailing of the international search report

11/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gamb, V

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/10253

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 770 629 A (UNION CARBIDE CHEM PLASTIC) 2 May 1997 see example 3 see claims 1,2 ---	1-10
A	EP 0 713 888 A (UNION CARBIDE CHEM PLASTIC) 29 May 1996 see example 8; table 5 see claims 1,4-9 -----	1-7,10

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 98/10253

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0691367 A	10-01-1996	US 5503914 A	02-04-1996
		AU 681033 B	14-08-1997
		AU 2489895 A	18-01-1996
		BR 9503246 A	23-04-1996
		CA 2153434 A	09-01-1996
		JP 8059910 A	05-03-1996
EP 0754708 A	22-01-1997	US 5677375 A	14-10-1997
		AU 6057996 A	30-01-1997
		CA 2181617 A	22-01-1997
		JP 9118722 A	06-05-1997
EP 0794200 A	10-09-1997	US 5665818 A	09-09-1997
		AU 1507397 A	11-09-1997
		CA 2199078 A	05-09-1997
		JP 10030009 A	03-02-1998
EP 0770629 A	02-05-1997	AU 7051596 A	01-05-1997
		CA 2188722 A	27-04-1997
		CZ 9603145 A	14-05-1997
		HU 9602981 A	28-10-1997
		JP 9165406 A	24-06-1997
		PL 316698 A	28-04-1997
		SK 138796 A	08-04-1998
EP 0713888 A	29-05-1996	US 5589539 A	31-12-1996
		AU 689334 B	26-03-1998
		AU 3799595 A	30-05-1996
		BR 9505265 A	16-09-1997
		CA 2163467 A	24-05-1996
		JP 8208738 A	13-08-1996